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LVIII. *Valve-generated Oscillations in Coupled Circuits.* *By* E. TAYLOR JONES, *D.Sc., F.Inst.P., Professor of Physics in the University College of North Wales, Bangor* *.

[Plate IV.]

1. THE present paper is mainly concerned with certain phenomena which occur when a high-tension transformer, an induction coil, or other coupled system in which the secondary circuit possesses considerable electrostatic capacity, is switched into a circuit in which oscillations of audible frequency are generated by a triode valve.

The diagram in fig. 1 shows one of the arrangements of apparatus employed in the experiments. A and B are the generating coils, connected in the anode and grid circuits respectively, $C_1$ is the primary condenser, $O_1$ a current oscillograph, H a hot wire ammeter, T the transformer † or induction coil which may be shortcircuited by the key K. $O_2$ is an electrostatic oscillograph connected with the secondary terminals of the transformer. The deflexion shown by $O_1$ is proportional to the current flowing through the instrument, that of $O_2$ to the square of the difference of potential at its terminals. In most of the experiments four 15-watt transmitting valves were used in parallel, with anode voltage

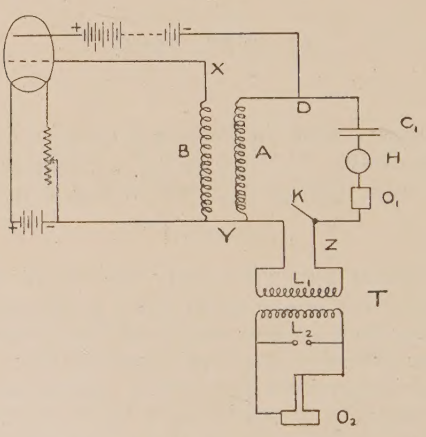
* Communicated by the Author.

† The high-tension transformer used in these experiments was kindly supplied by the Cox-Cavendish Electrical Company.

400, the anode current ranging up to 100 milliamperes. The shortcircuiting key K consisted of a mercury dipper interrupter actuated by the rotating mirror used with the oscillographs.

The oscillatory system thus consists of two coupled circuits of which the primary includes the coil A, the condenser $C_1$, the ammeter and oscillograph $O_1$, and the primary coil of the transformer. The capacity in the secondary circuit includes that of the oscillograph $O_2$ and spark-gap electrodes, and the distributed capacity of the coil, and may be increased by the addition of a variable condenser connected

Fig. 1.




to the secondary terminals. This system possesses two frequencies of oscillation which depend upon the inductances and capacities and upon the coupling of the two circuits. The coupling is less than that of the transformer alone in the ratio of $L_1$, the self-inductance of the primary coil, to $L_1 + L_A$, the total self-inductance in the primary circuit. Instead of the connexions shown in fig. 1 the condenser and transformer, with the ammeter and oscillograph, may be connected between the points D and X, in which case the coupling is further reduced owing to the addition of the coil B to the primary circuit.

The oscillation may be rendered audible by means of a telephone connected with a loop of wire loosely coupled with coil A.

The following are the effects which we shall consider:—

1. When the system is oscillating with the transformer in circuit one note only is usually heard in the telephone, not two notes simultaneously as might be expected. A similar effect is also observed in other coupled systems, electrical and mechanical (*e. g.* the singing arc with coupled circuits, and reed pipes), which are maintained in oscillation, but as far as the writer is aware this effect has not hitherto been satisfactorily explained*.
2. If the system is oscillating with the key K closed and the transformer is then thrown into the circuit, the pitch of the telephone note may rise, or fall, or it may undergo no change. These various results may be produced by suitably adjusting the capacity of the condenser $C_1$.
3. In the secondary circuit the potential produced at unshortcircuiting is generally much higher than that generated afterwards by the alternating current flowing in the transformer. In fact the valve may be unable to maintain any oscillation with the transformer in circuit (as for instance when the capacity $C_1$ is too great), and there may still be a high potential generated at the secondary terminals when the transformer is switched in.

Some of these effects are illustrated by the current oscillograms reproduced in figs. 2–8 (Pl. IV.). Fig. 2 is a typical curve showing the effect of throwing the transformer into circuit. In this case the pitch rose by about a major third at unshortcircuiting, and the sound was at the same time reduced in intensity as is indicated by the small amplitude of the maintained oscillations in the latter part of the curve†. Fig. 3 shows a similar effect but with a greater rise of pitch (in this case a minor sixth) at the introduction of the transformer. In

* A similar preference for one or other of the two vibrations of a coupled system may also be observed in the case of damped vibrations. This has been considered by M. Wien (*Ann. der Physik*, lxi. p. 162, 1897) from the point of view of the difference of the damping coefficients of the two component vibrations. In some respects, however, Wien's conclusions with regard to the damping are not in agreement with those arrived at later by Drude (*Ann. der Physik*, xiii. p. 512, 1904). Wien does not consider the case of maintained vibrations.

† The movement in all the oscillograms is from right to left. The lower curve indicates time intervals, each wave representing 1/768 second.

these two cases no spark appeared at the secondary terminals either at unshortcircuiting or afterwards. If the gap is reduced so as to allow a spark to appear at unshortcircuiting the amplitude of the curve falls much more rapidly to a smaller value, and afterwards declines slowly to its final value, as shown in fig. 4 (8·3 mm. spark). With a shorter gap (3·4 mm.) the final steady state is reached sooner, the shorter spark evidently taking more energy from the system (fig. 5). If the gap is still further reduced (or the current increased) so that sparking takes place freely under the maintained alternating current flowing in the transformer, the curve is as shown in fig. 6. It appears that each spark has the effect of reducing the amplitude of the oscillation, and that some time is required for it to recover and grow again to the value needed for a repetition of the discharge.

If the oscillograph, instead of being in the condenser circuit, is connected in the transformer primary circuit, as at Z (fig. 1), the instrument will of course show only the current flowing after the key K is opened (fig. 7).

The curve of fig. 8 was taken with an induction coil substituted for the transformer. On this occasion the condenser $C_1$ (2·63 mfd.) with the induction coil and oscillograph were connected between D and X (fig. 1). The curve indicates a fall of pitch of about a semitone at unshortcircuiting. Fig. 9 (Pl. IV.) shows the beginning of a train of oscillations (condenser, coil, and oscillograph between D and Y as in fig. 1) produced by closing a contact maker in the grid circuit.

It will be seen that all these curves show a single oscillation of increasing, diminishing, or constant amplitude when the transformer or induction coil is in circuit and not sparking, and that there is no evidence of a periodic fluctuation of amplitude such as might be expected in a system possessing two frequencies of oscillation.

We will now proceed to consider the reasons for the peculiar changes of pitch at unshortcircuiting, and for the almost complete absence of any trace of one or other of the two component oscillations of the system, both in the telephone sound and in the current oscillograph curves.

### 2. *The Apparent Self-Inductance and Resistance of the Primary Coil of a Transformer.*

In the first place it is necessary to consider certain points in the theory of the transformer regarded as a coupled system having electrostatic capacity in the secondary circuit,

to the primary of which an alternating potential of given frequency and constant amplitude is applied. Since the secondary capacity is in part distributed over the coil, and in consequence the current in the secondary wire varies along its length, we shall (after Drude *) employ a symbol ($i_2$) to represent the current in the central winding of the secondary coil, and shall denote by $L_{21}$ the coefficient of induction of the primary on the secondary, by $L_{12}$ that of the secondary on the primary. The E.M.F. applied to the primary terminals having frequency $p/2\pi$ and amplitude E, the equations for the primary and secondary currents are

$$L_1\frac{di_1}{dt} + L_{12}\frac{di_2}{dt} + R_1 i_1 = E\, e^{ipt}, \quad . \quad . \quad . \quad (1)$$

$$L_2\frac{di_2}{dt} + L_{21}\frac{di_1}{dt} + R_2 i_2 + V_2 = 0, \quad . \quad . \quad . \quad (2)$$

where $V_2$ is the potential at the secondary terminals. Also, if $C_2$ is the secondary capacity,

$$i_2 = C_2\frac{d\,V_2}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Assuming that in the forced oscillation $i_1$ and $i_2$ vary as $e^{ipt}$, and eliminating $i_2$ and $V_2$, we arrive after reduction at the equation for $i_1$,

$$L\frac{di_1}{dt} + R\, i_1 = E\, e^{ipt}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$L = L_1 + \frac{L_{21}L_{12}p^2C_2(1-p^2L_2C_2)}{(1-p^2L_2C_2)^2 + R_2^2C_2^2p^2}\,\dagger, \quad . \quad . \quad (5)$$

$$R = R_1 + \frac{L_{21}L_{12}p^4C_2^2R_2}{(1-p^2L_2C_2)^2 + R_2^2C_2^2p^2}\,\dagger. \quad . \quad . \quad . \quad (6)$$

Introducing the coupling of the transformer $k^2$ ($=L_{21}L_{12}/L_1L_2$), and denoting $p^2L_2C_2$, the ratio of the squares of the applied frequency and the natural frequency of the secondary circuit when oscillating alone, by $f$, and

* *Ann. d. Physik*, xiii. p. 517 (1904).

† These expressions may be deduced from those given in Professor Gray's 'Absolute Measurements in Electricity and Magnetism,' pp. 251, 252 (1921), for the more general case in which there is capacity in both primary and secondary circuits.

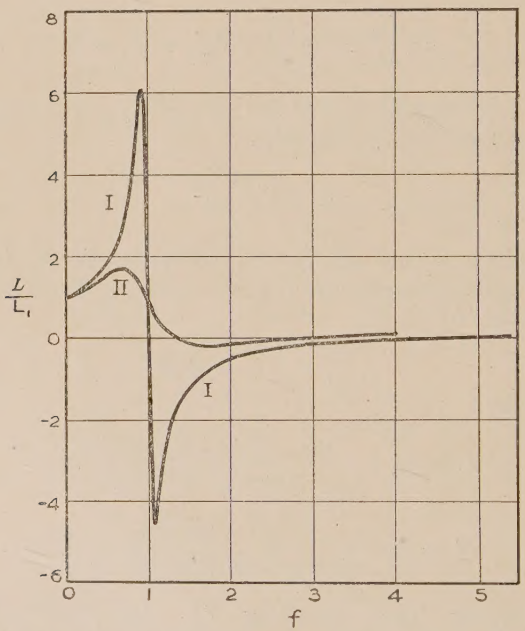
the quantity $\left(\frac{R_2}{L_2}\right)^2 L_2C_2$ by $\lambda$, we find for $L$ and $R$ the expressions

$$L = L_1\left[1+\frac{k^2f(1-f)}{(1-f)^2+\lambda f}\right], \quad . \quad . \quad . \quad . \quad (7)$$

$$R = R_1\left[1+\frac{k^2\frac{L_1}{R_1}\frac{R_2}{L_2}f^2}{(1-f)^2+\lambda f}\right]. \quad . \quad . \quad . \quad (8)$$

$L$ and $R$ may be called respectively the "apparent self-inductance" and the "apparent resistance" of the primary coil of the transformer. They are the self-inductance and

Fig. 10.




resistance which a single coil would require to have in order to allow, under the action of the applied E.M.F. $E\cos pt$, a current $i_1$ to pass identical in amplitude and phase with the primary current of the transformer. The apparent impedance of the primary coil is $\sqrt{R^2+L^2p^2}$, and the angle by which the primary current is behind the applied E.M.F. in phase is $\tan^{-1} Lp/R$.

It appears from the expression (7) that $L$ is equal to $L_1$

when the applied E.M.F. is varying infinitely slowly ($f=0$), and again in the case of resonance ($f=1$). For infinitely rapid variations ($f=\infty$) $L$ is equal to $L_1(1-k^2)$.

The manner of variation of $L$ with the applied frequency may be illustrated by a numerical case. For the induction coil used in the present experiments the coupling $k^2$ was 0·768, and in certain circumstances $\lambda$ was 0·005147. These values being assumed, the variation of the ratio $L/L_1$ with $f$ is shown in fig. 10, curve I. It will be seen from this curve that as the applied frequency increases from zero, $L/L_1$ increases from unity to a maximum of 6·16 at $f=0·93$, then rapidly diminishes and becomes zero at a value of $f$ slightly greater than unity (1·00676). Between this value of $f$ and 4·281, $L$ is negative, the greatest negative value being $4·547\,L_1$ at $f=1·08$. With further increase of $f$, $L/L_1$ becomes and remains positive, slowly approaching its final value 0·232.

The form of the curve in the neighbourhood of the resonance point ($f=1$) depends greatly upon the value of the coefficient $\lambda$, which is proportional to the square of the resistance of the secondary circuit. If $R_2$ be regarded as the effective resistance of the secondary, as determined from the damping of its oscillation when the primary is on open circuit, the value of $\lambda$ may vary considerably with the conditions of the experiment. Curve II. in fig. 10 shows the variation of $L/L_1$ when $\lambda$ is 0·174, a value determined for the same induction coil in different circumstances. In this case $L$ is negative between the values 1·338 and 3·222 of $f$, but the variation of $L$ is now much smaller and more gradual near the resonance point. The greatest positive value of $L/L_1$ is 1·761 at $f=0·7$, the greatest negative value 0·163 at $f=1·7$. The effect of increasing the resistance of the secondary circuit is to diminish the range of variation of $L$, and also to diminish the range of frequencies over which $L$ is negative.

If $\lambda$ is increased beyond a certain point the $L/L_1$ curve fails to intersect the horizontal axis, and $L$ can no longer have negative values. The limiting value of $\lambda$ may be found by equating to zero the expression for $L$ given in (7). The coupling $k^2$ being always less than unity, the conditions that the equation for $f$ should have real positive roots are

$$(\lambda+k^2)^2 \not< 4\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\lambda+k^2 < 2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The greatest value of $\lambda$ that satisfies these conditions is

$$\lambda = 2-k^2-2\sqrt{1-k^2}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

With $k^2=0{\cdot}768$, this gives $0{\cdot}2686$ as the greatest value of $\lambda$ which allows $L$ to become zero. At this value of $\lambda$ the $L/L_1$ curve touches the horizontal axis at the point

$$f = 1/\sqrt{1-k^2}.$$

If the resistance of the secondary circuit is so small that $\lambda$ is negligible the expression (7) reduces to

$$L = L_1\left(1+\frac{k^2 f}{1-f}\right), \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which becomes infinite with change of sign at the resonance point, and changes sign again at $f=1/(1-k^2)$.

According to (7) the effect of an increase of the coupling is in general to increase the variation of $L$, and also to increase the range of frequencies over which $L$ is negative. By (11) it also increases the maximum value of $\lambda$ which allows $L$ to change sign.

In the valve experiment the rise of pitch sometimes heard in the telephone when the transformer is unshortcircuited is accounted for by the fact that the apparent self-inductance of the transformer primary is negative at certain frequencies. If the frequency with the transformer in circuit lies within the range over which $L$ is negative the frequency will increase because of the diminution of self-inductance of the whole oscillatory circuit when the transformer is introduced.

In one experiment, in which the connexions were as in fig. 1, the pitch of the note was observed to fall slightly ($L$ positive) when the induction coil was switched in if the capacity $C_1$ was less than about $0{\cdot}19$ mfd.; at this value the pitch was the same whether the coil was in circuit or not, indicating that $L$ was zero. If $C_1$ was between $0{\cdot}19$ and $0{\cdot}902$ mfd. the pitch rose at unshortcircuiting ($L$ negative), the rise of pitch at the latter value being about a semitone. The self-inductance of coil A in this experiment was $0{\cdot}086$ henry, so that a rise of pitch of a semitone indicates the addition to the circuit of a self-inductance of about $-0{\cdot}01$ henry. When $C_1$ was further slightly increased the pitch fell at the introduction of the coil by about the same interval, indicating a positive value for $L$, but it was noticed that the diminution of intensity of the sound at unshortcircuiting was considerably greater now than when $L$ was negative. The current flowing in the oscillatory circuit was therefore considerably reduced in these circumstances, that is, just after $L$ changed from a negative to a positive

value *. At still greater values of $C_1$ a fall of pitch similar in amount was heard when the coil was thrown into circuit.

If $C_1$ is increased from a small value with the induction coil always in circuit, the pitch falls gradually until a certain stage is reached at which a fall of a full tone occurs very rapidly. With about 0·9 mfd. in circuit this fall of pitch can be produced by as small a change as 0·002 mfd. in the value of $C_1$. With further increase of $C_1$ the pitch gradually falls. The experiment may be varied by first adjusting $C_1$ nearly to the critical value, when a slight change of the filament current produces the sudden change of pitch. A change in the filament current alters the current in the oscillatory circuit, and therefore also the inductances of the induction-coil circuits. Probably this effect is more marked in the secondary than in the primary, since the latter circuit contains also considerable air-core inductance. In this way a very gradual variation of the tuning of the circuits can be effected. Occasionally the two notes, separated by a finite interval, were heard together in the telephone when the filament current was adjusted to a certain value.

In another experiment, with a different pair of generating coils and with the condensers and induction coil connected to the point X (fig. 1), matters proceeded rather differently when $C_1$ was varied. At 0·85 mfd., with the induction coil in circuit, a clear note was heard in the telephone, and the change of pitch at shortcircuiting indicated that $L$ was negative. At 1·56 mfd. the note was about a perfect fifth lower in pitch, and at this value $L$ was positive. But no note at all was heard with the inductance coil in circuit if $C_1$ was between these two values. It appears therefore that, in addition to the break of continuity in the variation of frequency which occurs when $C_1$ is gradually increased, there may also be an interval in the sequence of values of the capacity at which oscillations are audibly produced by the system. These effects will be considered later from another point of view, in connexion with the frequencies of the whole oscillatory circuit regarded as a coupled system.

When the high-tension transformer was substituted for the induction coil the rise of pitch at unshortcircuiting could be made much greater. Thus with $L_A = 0{\cdot}086$ henry and $C_1 = 3{\cdot}5$ mfd. the rise of pitch was about a minor sixth (see fig. 3), indicating an apparent self-inductance of about

* In the circumstances of this experiment the core of the induction coil was in a state well below that of maximum inductance, so that a diminution of current was accompanied by a diminution of $L_1$.

$-0{\cdot}052$ henry. The value of the coefficient $\lambda$ for the transformer in the circumstances of this experiment was about 0·52. It may be found from the period and decrement of the oscillation of the secondary circuit with the primary open. Such oscillations may be produced by means of a battery and interrupter (without condenser) in the primary circuit. An oscillation of this kind (as shown by the electrostatic oscillograph) is given in fig. 11 (Pl. IV.), but the form of the curve, and in particular the ratio of the periods of the two half-waves which appear in it, varied considerably with the current used in starting the oscillations, as might be expected owing to the very variable inductance of a coil provided with a closed iron core. If the above value be assumed for $\lambda$ it follows from condition (9) that the coupling of the transformer circuits must be at least as great as 0·92.

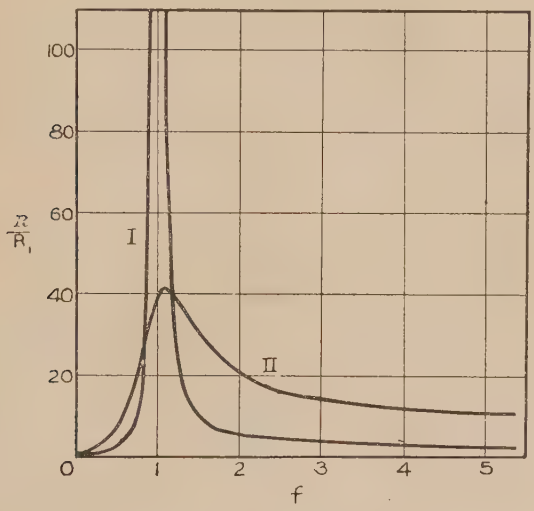
With the valves and coils used in these experiments it was not found possible to reduce the frequency sufficiently to produce with the transformer a discontinuity of pitch similar to that observed with the coil.

The experiments may be modified by connecting a variable condenser to the secondary terminals of the transformer. If $C_2$ is increased, both $\lambda$ and $f$ increase, and the effect is somewhat similar to that of diminishing $C_1$. The primary capacity being kept constant, if $C_2$ is small the apparent inductance of the transformer is negative, if $C_2$ is large $L$ is positive. At a certain value of the secondary capacity no change of pitch occurs when the transformer is short-circuited.

Turning now to the apparent resistance of the primary coil as given by (8), the variation of $R/R_1$ with $f$ is shown in fig. 12 for the two numerical cases of fig. 10, the value of $R_1/L_1$ being taken as 149 in both cases. Curve I. is the curve for the smaller secondary resistance. In this case the ratio $R/R_1$ is unity at very low frequency, 2·109 at very high frequency, and has a sharp maximum of 216·3 (not shown in the diagram) at a frequency slightly greater than the resonance value. In curve II., calculated for the higher secondary resistance, the variation is much more gradual, the maximum being about 41·6 at $f=1{\cdot}1$, but the region of high apparent resistance extends to frequencies differing more widely from the resonance value. The fact that the apparent resistance of the primary coil of a transformer may be very great at and near the resonance frequency is of fundamental importance in connexion with the question, to

be discussed later, of the maintenance of the oscillations of the whole coupled system.

Fig. 12.




### 3. *Energy Relations.*

It is of interest to consider the energy relations of the transformer system in connexion with the apparent inductance and resistance of the primary. Since $L$ is sometimes negative it is clear that the expression $\frac{1}{2}Li_1^2$ cannot represent the electrokinetic energy of the transformer circuits, or the total energy of the circuits, both of which quantities are always positive. To simplify the matter we will suppose that $L_{12}=L_{21}=M$, and in the first place neglect the resistances.

Equation (4) may now be written

$$L\frac{di_1}{dt}=E\cos pt, \quad \ldots\ldots \quad (13)$$

and by (2) and (3)

$$i_2=\frac{MC_2p^2}{1-f}i_1. \quad \ldots\ldots \quad (14)$$

The electrokinetic energy of the primary coil is therefore

$$\begin{aligned}\tfrac{1}{2}i_1(L_1i_1+Mi_2)&=\tfrac{1}{2}i_1^2\left(L_1+\frac{M_2C_2p^2}{1-f}\right)\\&=\tfrac{1}{2}L_1i_1^2\left(1+\frac{k^2f}{1-f}\right)\\&=\tfrac{1}{2}Li_1^2 \quad \ldots\ldots \quad (15)\end{aligned}$$

by (12).

The electrostatic energy in the secondary circuit expressed in terms of the primary current is

$$\tfrac{1}{2}C_2V_2^2 = \frac{1}{2}\frac{k^2L_1 f}{(1-f)^2}(i_0^2 - i_1^2), \quad . \quad . \quad . \quad (16)$$

where $i_0$ is the maximum value of the primary current.

Substituting from (14) and (16) in the expression for the total energy of the transformer circuits, we find after reduction

$$\tfrac{1}{2}L_1i_1^2 + Mi_1i_2 + \tfrac{1}{2}L_2i_2^2 + \tfrac{1}{2}C_2V_2^2 = \tfrac{1}{2}Li_1^2 + \frac{1}{2}\frac{k^2L_1 f}{(1-f)^2}i_0^2, \quad . \quad . \quad (17)$$

The second term on the right-hand side of (17) represents the electrostatic energy in the secondary circuit at the moment when the primary current is zero, and it is then the total energy of the transformer system.

From (15) and (17) we see that the expression $\frac{1}{2}Li_1^2$ may be regarded as representing (1) the electrokinetic energy of the primary coil of the transformer, (2) the increase of the total energy of the transformer circuits during the growth of the primary current from 0 to $i_1$. Both of these statements are consistent with the result that by (13) the work done on the system by the applied E.M.F. during the growth of the primary current from 0 to $i_1$ is $\frac{1}{2}Li_1^2$.

Now bringing in the resistances we will calculate the total energy dissipated in the transformer circuits during one period T of the forced oscillation. If $t$ be measured from a moment at which the primary current is zero, the expression for this current may be written

$$i_1 = A \sin pt.$$

The energy dissipated in the primary circuit is

$$\int_0^T R_1i_1^2\,dt = R_1i_s^2\,T,$$

$i_s$ being the R.M.S. primary current.

The secondary current is given by

$$i_2 = \frac{Mp^2C_2}{\{(1-f)^2+\lambda f\}^{1/2}} A \sin(pt-\gamma),$$

where

$$\tan\gamma = \frac{R_2C_2p}{1-f}.$$

The energy dissipated in the secondary circuit during one period is therefore

$$\int_0^{\mathrm{T}} \mathrm{R}_2 i_2^2 dt = \frac{\mathrm{T}}{2} \frac{\mathrm{R}_2 k^2 \mathrm{L}_1 \mathrm{L}_2 \mathrm{C}_2{}^2 p^4 \mathrm{A}^2}{(1-f)^2+\lambda f}$$
$$= \frac{\mathrm{R}_2}{\mathrm{L}_2} \cdot \frac{k^2 \mathrm{L}_1 f^2}{(1-f)^2+\lambda f} i_s{}^2 \mathrm{T}.$$

Consequently the total energy dissipated in one period is

$$\int_0^{\mathrm{T}} (\mathrm{R}_1 i_1{}^2 + \mathrm{R}_2 i_2{}^2)\, dt = \mathrm{R}_1 \left\{ 1 + \frac{k^2 \frac{\mathrm{L}_1}{\mathrm{R}_1} \cdot \frac{\mathrm{R}_2}{\mathrm{L}_2} f^2}{(1-f)^2+\lambda f} \right\} i_s{}^2 \mathrm{T}$$
$$= R i_s{}^2 \mathrm{T}. \quad \ldots\ldots \text{ by (8).}$$

The expression $Ri_s^2$ therefore represents the mean rate of dissipation of energy in both circuits of the transformer during the forced oscillations. It also represents the mean rate at which work must be done on the system by the applied E.M.F. in order to maintain the oscillations. If $R$ is very great, as it may be when the frequency is near the resonance value, it is clear that a valve, to which energy is supplied at a limited rate, may for this reason fail to maintain oscillations of appreciable amplitude in the transformer.

### 4. *The Oscillatory Circuit as a Coupled System.*

In considering the action of the transformer we have regarded this portion of the oscillatory circuit as executing forced oscillations under the action of an applied E.M.F. of frequency $n$ $(=p/2\pi)$. When we deal with the whole oscillatory circuit, however, we must regard $n$ as a natural frequency, since it is determined almost entirely by the constants of the circuit.

The system possesses two natural frequencies of oscillation given (if resistances are neglected) by the well-known equation

$$8\pi^2 n^2 = \frac{1}{1-\mathrm{K}^2} \left\{ \frac{1}{l_1 \mathrm{C}_1} + \frac{1}{\mathrm{L}_2 \mathrm{C}_2} \right.$$
$$\left. \pm \sqrt{\left( \frac{1}{l_1 \mathrm{C}_1} - \frac{1}{\mathrm{L}_2 \mathrm{C}_2} \right)^2 + 4\mathrm{K}^2 \frac{1}{l_1 \mathrm{C}_1} \frac{1}{\mathrm{L}_2 \mathrm{C}_2}} \right\}, \quad (18)$$

where $l_1$ is the self-inductance of the primary circuit, $\mathrm{L}_1 + \mathrm{L}_\mathrm{A}$, and $\mathrm{K}^2$ is the coupling of the two circuits forming the whole system, *i. e.*

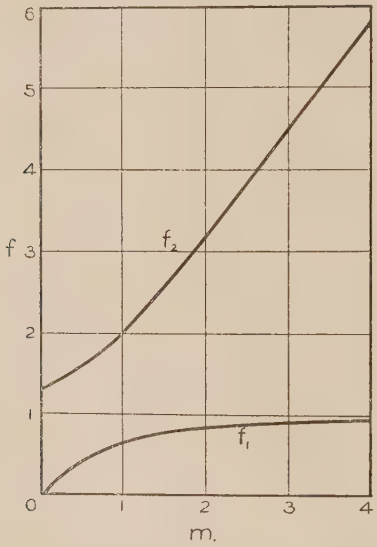
$$\mathrm{K}^2 = \mathrm{L}_{21}\mathrm{L}_{12}/l_1 \mathrm{L}_2.$$

If $L_2C_2/l_1C_1$ be denoted by $m$, the ratios of the squares of the frequencies of these oscillations to the square of the frequency of the secondary circuit when oscillating alone are given by

$$\left.\begin{aligned} f_1 = 4\pi^2 n_1^2 L_2C_2 &= \frac{1}{2(1-K^2)}\left\{m+1-\sqrt{(m-1)^2+4K^2m}\right\} \\ f_2 = 4\pi^2 n_2^2 L_2C_2 &= \frac{1}{2(1-K^2)}\left\{m+1+\sqrt{(m-1)^2+4K^2m}\right\} \end{aligned}\right\}. \quad . \quad . \quad . \quad (19)$$

The manner in which $f_1$ and $f_2$ vary with $m$ is illustrated by the two curves in fig. 13, which represent values calculated

Fig. 13.




from (19) for the particular case $K^2=0{\cdot}26$, the coupling found for one of the arrangements used in the present experiments. The curves show that $f_1$ and $f_2$ continually increase as $m$ increases from zero. At first $f_1$ increases rapidly, afterwards more slowly, gradually approaching unity, but only attaining this value when $m$ becomes infinite. On the other hand, $f_2$ begins at the value $1{\cdot}3514$ $\left(i.e.\ \frac{1}{1-K^2}\right)$ and increases to infinity as $m$ indefinitely increases.

It appears therefore that the system (supposed to have

resistances too small to affect the frequencies appreciably) never oscillates with a frequency lying between the values $1/2\pi\sqrt{L_2C_2}$ (the resonance frequency of the transformer) and $1/2\pi\sqrt{L_2C_2(1-K^2)}$, but that the frequency may have any value lying outside these limits*. Also the resonance frequency ($f=1$) only appears when $m$ is very great, *e. g.* when $C_1=0$, that is, when the primary is on open circuit. It follows also that if the system oscillates with a frequency less than the resonance frequency of the transformer ($f<1$), this oscillation must be the slower of the two oscillations of the system; if the observed frequency is greater than the resonance value ($f>1$) this must be the more rapid component.

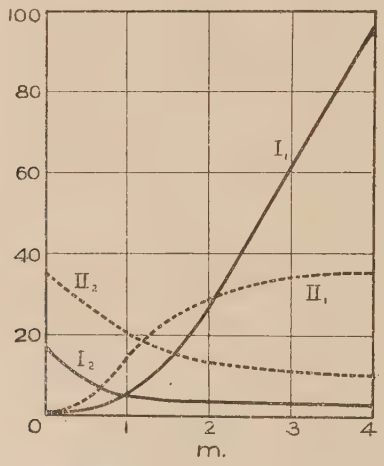
What happens in the valve experiment described on p. 633 is that when $C_1$ is increased from a small value ($m$ diminishing) the note heard at first is the higher note of the system, but at a certain value of $m$ not far from unity the note suddenly changes into the lower component and there is a sudden fall of pitch determined by the ratio of the two values of $f$ for the value of $m$ at which the change takes place.

It remains to be explained, however, why the two notes are not generally produced together, and why the lower note is heard when $m$ is small ($C_1$ large), the higher note when $m$ is large. For this purpose it is necessary to know the values of $R$, the apparent resistance of the transformer primary for various corresponding values of $f_1$ and $f_2$. Taking again the two numerical cases of figs. 10 and 12, the values of $R$ were calculated for the $f_1$ and $f_2$ corresponding to various values of $m$ as shown in fig. 13. The results are shown in fig. 14, in which the full-line curves refer to the smaller secondary resistance ($\lambda=0{\cdot}005147$). In fig. 14 curve $I_1$ shows values of $R/R_1$ for the oscillation of lower frequency ($n_1$) of the system, curve $I_2$ for the higher frequency ($n_2$). The curves extend over the range $m=0$ to $m=4$. It will be seen that when $m$ is small the apparent resistance of the transformer primary is greater for the higher frequency than for the lower; when $m$ is large $R$ is greater for the lower frequency. The curves intersect at a value of $m$ slightly greater than 1, and the values of $R$ are varying rapidly at the point of

* It may be noticed that the range $f=1$ to $f=1/(1-K^2)$ is also that over which the apparent self inductance of the *whole oscillatory circuit* (excluding the condenser $C_1$) is negative. This follows from equation (12) on substitution of $K^2$ for $k^2$.

intersection. Thus at $m=1{\cdot}1$ the apparent resistance is nearly 40 per cent. greater for the lower frequency component than for the higher; at $m=0{\cdot}9$ the apparent resistance is greater for the more rapid component in about the same ratio. At values of $m$ more remote from unity the values of $R$ for the two oscillations of the system differ much more. Thus at $m=1{\cdot}5$, $R$ is 3·5 times as great for the slower oscillation as for the more rapid; at $m=0{\cdot}5$, $R$ is over five times as great for the quicker component as for the slower. At the point of intersection the two equal values of $R$ are each about $5{\cdot}2\,R_1$.

Fig. 14.




The broken line curves $II_1$, $II_2$ in fig. 14 refer to the other numerical case ($\lambda=0{\cdot}174$). These curves present similar features; when $m$ is small the apparent resistance is much greater for the quicker component, when $m$ is large it is much smaller for this component. The point of intersection of the curves $II_1$, $II_2$, occurs at a value of $m$ slightly greater than 1·2, the equal values of $R$ being about $18{\cdot}5\,R_1$. It appears that the value of $m$ at which the apparent resistance of the transformer primary is the same for the two oscillations of the system is rather greater than unity, its excess above this value increasing with the resistance of the secondary coil.

When we remember that the condition for maintenance of valve oscillations depends upon the resistance of the oscillatory circuit — the addition of a few ohms to this

circuit is in some cases sufficient to stop the oscillations altogether,—it is easy to understand from the curves of fig. 14 why only one oscillation is usually maintained at a time, not both together, and why the slower component is the favoured one if $m$ is small, the other if $m$ is large *.

If the two oscillations of the system are ever maintained simultaneously this can only occur when the two values of $R$ are equal or nearly so, that is, at the point of intersection of the curves,† and then only if the value of $R$ at the intersection is not too great. If $R$ is too great at the intersection no oscillations may be produced in appreciable intensity unless $m$ is either considerably smaller or considerably greater than unity.

Since the frequency ratio $n_2/n_1$ of a system having given coupling is smallest when $m=1$, we may conclude that the two oscillations of the system can only be maintained simultaneously when the ratio of their frequencies is nearly at its minimum.

In former papers ‡ the writer has shown that similar effects are produced when a pair of coupled oscillatory circuits are associated with a singing arc. In this arrangement also one note only is, as a rule, produced, this being the lower note of the system if $m$ has less than a certain value (not far from unity), and the higher note if $m$ is greater than the critical value. In certain cases both notes may be produced simultaneously (*loc. cit.* p. 719), accompanied by their difference-tone, which is unusually prominent in these circumstances.

An examination of the curves of fig. 13 shows that if the telephone note undergoes no change of pitch when the transformer is switched into the circuit of fig. 1, this can

* It is well known that a valve fails to generate oscillations if the self-inductance in the primary circuit exceeds a certain value depending upon the other constants of the circuit. It might therefore be thought that the extinction of one of the component oscillations is due to the increase of $L$ near the resonance point (see fig. 10). This supposition would, however, not account for the facts. For if $L$ is large and positive, $f$ must be less than 1, and the frequency must consequently be that of the slower component (see fig. 13). If the increased apparent self-inductance of the transformer primary were the cause of the extinction of one of the notes, this would always be the lower note.

† It is assumed that $R_1$ is not extremely small.

‡ Phil. Mag. Jan. 1909, p. 41; Nov. 1909, p. 713 (with M. Owen); Oct. 1910, p. 660 (with D. E. Roberts).

only happen if the frequency before admission of the transformer is identical with that of the quicker component of the vibration afterwards, since $L$ is zero only at values of $f$ greater than unity. It can also be easily verified, if resistances are neglected, that the condition $L=0$, *i. e.*

$$1+\frac{k^2 f}{1-f}=0,$$

is consistent with the condition that the frequency $1/2\pi\sqrt{L_A C_1}$ should be equal to the greater of the two frequencies ($n_2$) given by equation (18).

The explanation given above of the absence of one or other of the two component vibrations of the system applies only to the steady state some time after unshortcircuiting when the amplitude has become constant. In the period of transition following the introduction of the transformer, however, while the system is accommodating itself to its new conditions, there is evidence that the two components often exist together. This matter we will now proceed to consider.

### 5. *Transient Effects of throwing the Transformer into Circuit.*

We will suppose that the transformer is unshortcircuited at a moment when the condenser $C_1$ is at its maximum potential. At this instant there is no current or potential in the secondary circuit, and the conditions are very similar to those existing in the Tesla coil, which is excited by charging the condenser to a certain initial potential $V_0$ and allowing it to discharge through the primary coil.

Neglecting for the present the action of the valve in maintaining (or reducing the damping of) one or other of the two oscillations, we should expect that two damped oscillations are set going, the potential at the secondary terminals being given by the expression *

$$V_2=\frac{L_2 C_1 V_0}{\{(l_1 C_1-L_2 C_2)^2+4K^2 l_1 C_1 L_2 C_2\}^{1/2}}\{e^{-k_1 t}\cos(2\pi n_1 t+e_1)-e^{-k_2 t}\cos(2\pi n_2 t+e_2)\},\quad .\quad .\quad (20)$$

* Drude, *l. c.* p. 539.

where

$$k_1 = 4\pi^2 n_1^2\left(\frac{\theta_1+\theta_2}{2}-\beta\right),$$

$$k_2 = 4\pi^2 n_2^2\left(\frac{\theta_1+\theta_2}{2}+\beta\right),$$

$$\theta_1 = \tfrac{1}{2}r_1C_1, \qquad \theta_2 = \tfrac{1}{2}R_2C_2,$$

$$\beta = -\frac{2\pi^2 n_1^2 n_2^2}{n_2^2-n_1^2}(\theta_1-\theta_2)(l_1C_1-L_2C_2),$$

$$\sin e_1 = \frac{2\beta+\dfrac{n_2-n_1}{n_2}\delta}{\dfrac{n_2-n_1}{2\pi n_1 n_2}-4\pi\beta n_1\delta},$$

$$\sin e_2 = \frac{2\beta+\dfrac{n_2-n_1}{n_1}\delta}{\dfrac{n_2-n_1}{2\pi n_1 n_2}-4\pi\beta n_2\delta},$$

$$\delta = \frac{\theta_1+\theta_2}{2}+\beta\frac{n_2-n_1}{n_2+n_1},$$

and $r_1$ is the resistance of the whole primary circuit.

According to (20) the two components of the wave of secondary potential have equal initial amplitudes and different damping factors. In the primary circuit also we should expect the wave-forms of potential and current to consist of two components having damping factors $k_1$ and $k_2$ and different initial amplitudes. It can be shown that the initial amplitudes of the components in the primary current variation are

$$\text{and} \quad \left.\begin{array}{l} \dfrac{2\pi n_1^3(4\pi^2 n_2^2 l_1C_1-1)}{n_2^2-n_1^2}\,V_0 \\ \dfrac{2\pi n_2^3(1-4\pi^2 n_1^2 l_1C_1)}{n_2^2-n_1^2}\,V_0. \end{array}\right\} \quad . \quad . \quad . \quad (21)$$

Fig. 15 (Pl. IV.) is an example of the curves shown by the electrostatic oscillograph, connected to the secondary terminals as in fig. 1, when the key K was opened. In this experiment the induction coil was used in place of the transformer owing to its greater suitability for inductance measurements. The periodic variations of amplitude in the curve of fig. 15 show clearly that two oscillations differing in frequency are present in the wave of secondary potential following the admission of the induction coil into the circuit.

The wave form shows considerable variations however, depending upon the phase of the previously existing oscillation at which the induction coil is switched in. If contact is broken at K at a moment when current is flowing into the condenser, a spark appears at the interrupter and the amplitude of the curve is small. The amplitude is greatest when contact is broken at a moment of maximum potential in $C_1$, and when consequently no spark appears at K. The curve shown in fig. 15 was the curve of greatest amplitude among twenty photographs obtained with a certain combination of coils and condensers, all taken with the same current (indicated by a hot-wire ammeter) flowing in the condenser circuit before admission of the induction coil.

The constants of the circuits were determined for about the mean currents flowing in the circuits during the decay of the oscillations *, and found to be as follows :—

$$l_1C_1 = 6{\cdot}728\,.\,10^{-8} \text{ c.g.s.}, \quad L_2C_2 = 1{\cdot}014\,.\,10^{-7} \text{ c.g.s.}$$
$$L_{21} = 4{\cdot}0 \text{ henries}, \quad K^2 = 0{\cdot}26.$$
$$r_1/l_1 = 384, \quad R_2/L_2 = 1310.$$

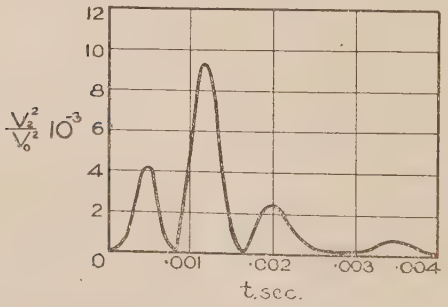
Calculated from these numerical values, the frequencies of the system are, by (18),

$$n_1 = 441{\cdot}7, \qquad n_2 = 806{\cdot}7,$$

and the expression (20) for the secondary potential becomes

$$V_2 = 95{\cdot}5V_0 e^{-383t}\cos(159000t + 1{\cdot}2)^\circ$$
$$-95{\cdot}5V_0 e^{-761t}\cos(290400t - 3{\cdot}55)^\circ. \quad . \quad . \quad (22)$$

Fig. 16.



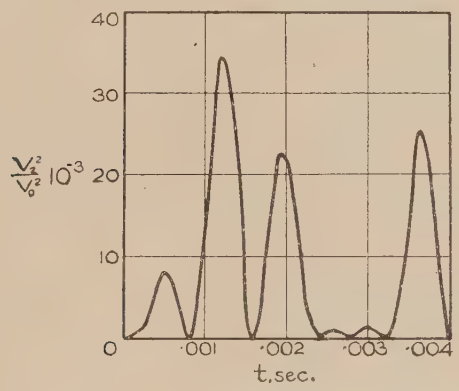

In fig. 16 is shown the curve representing values of $V_2^2/V_0^2$ calculated from (22) for various values of $t$, the time in seconds after admission of the induction coil. The

* Methods for determining the constants are given in 'The Theory of the Induction Coil,' Chap. VII. (1921).

curve indicates a maximum potential of $96{\cdot}4V_0$ at the second peak, but the relative heights of the successive peaks in this curve do not agree well with those of the photograph in fig. 15.

For comparison, the curve was also calculated without allowance for damping ($k_1=k_2=0$). This undamped curve is shown in fig. 17. It indicates a much higher maximum potential, viz. $185{\cdot}7V_0$, and a very different relation among the successive peaks.

Fig. 17




It is clear that fig. 17 indicates too high a maximum potential since it neglects damping altogether, while the maximum in fig. 16 is too small since it takes no account of the action of the valve in tending to maintain the more rapid oscillation. In the circumstances of the experiment the valve was unable to maintain this oscillation at a constant amplitude, but it considerably reduced its decrement.

The best plan that suggested itself at this stage was to determine the decrement $k_2$ of the rapid component directly from the curve of primary current (similar to fig. 3), since this curve apparently showed a single damped oscillation of frequency $n_2$. When this curve was carefully examined it indicated a frequency 807·4, which agrees satisfactorily with the calculated value of $n_2$ stated above (806·7); but its decrement showed considerable irregularity which may have been due to a slower superposed oscillation of small amplitude.

By (21) the ratio of the initial amplitudes of the slow and

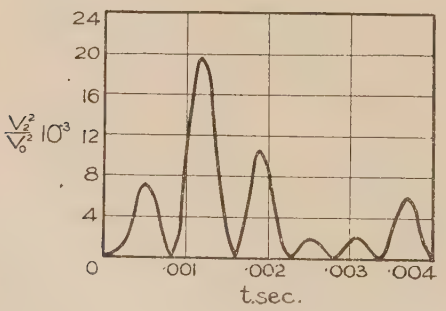
rapid components in the primary current wave is

$$\frac{n_1^3}{n_2^3} \cdot \frac{4\pi^2 n_2^2 l_1 C_1 - 1}{1 - 4\pi^2 n_1^2 l_1 C_1}.$$

In the present case this fraction is equal to 0·248, so that the initial amplitude of the slower component in the primary current is only about a quarter of that of the rapid component, while its decrement is considerably the greater of the two. The observed irregularities in the decrement of the current curve were, however, not quite so great as might be expected to arise from a superposed oscillation of frequency 441·7, damping factor 383, and initial amplitude one quarter of that of the rapid component.

The mean decrement determined from the first two periods of the current curve, covering the time occupied by the first group of waves in fig. 17, was 105. With this value of $k_2$ employed in the calculation (instead of 761) and all other coefficients as in (22), the calculated curve becomes that shown in fig. 18. The agreement with the photographed

Fig. 18.




curve of fig. 15 is now much closer, though the damping of the rapid component in fig. 18 is still rather overestimated.

The maximum potential indicated in fig. 18 is $140{\cdot}3V_0$, $V_0$ being the maximum potential of the primary condenser in the oscillations preceding the admission of the induction coil.

Now the smallest R.M.S. current which was observed to give at unshortcircuiting a 1 cm. spark between two metal spheres of 2 cm. diameter connected with the secondary terminals was 1·57 amperes. Also the frequency

Fig. 2.

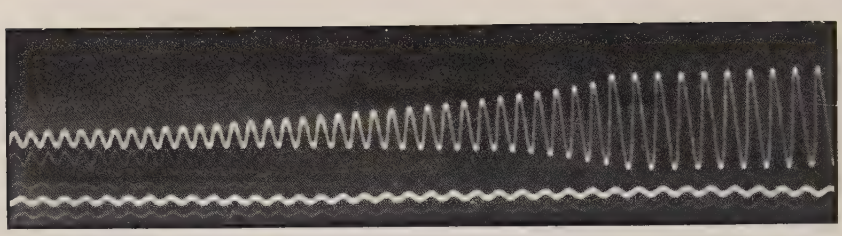


Fig. 3.

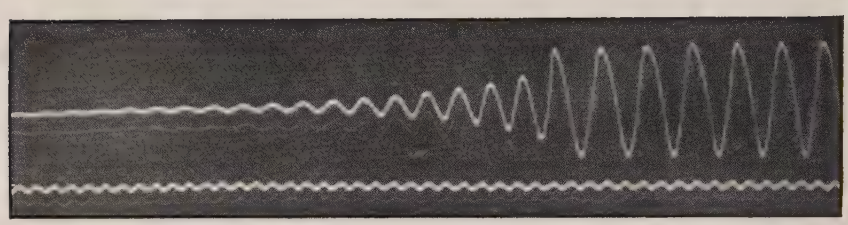


Fig. 4.

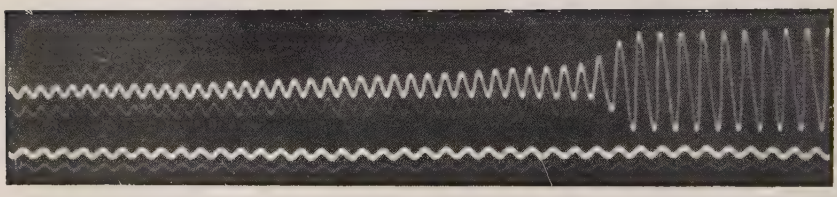


Fig. 5.

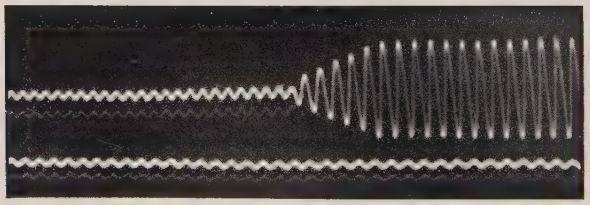


Fig. 6.

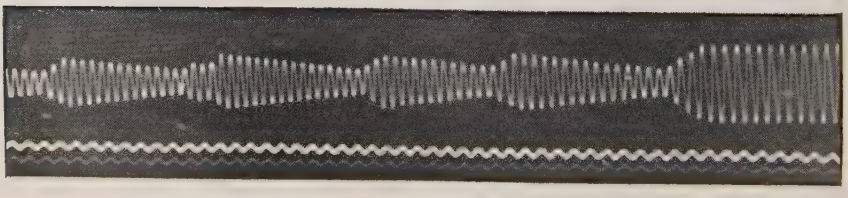


Fig. 7.

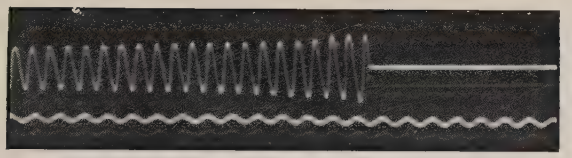


Fig. 8.

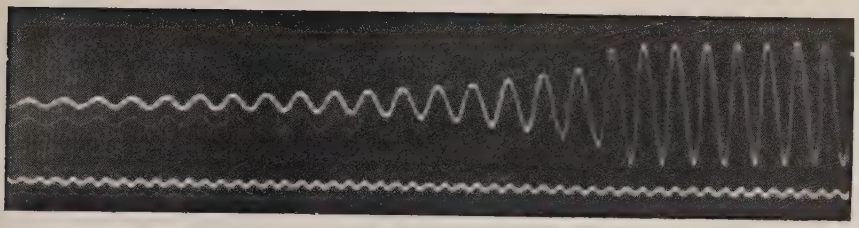


Fig. 9.

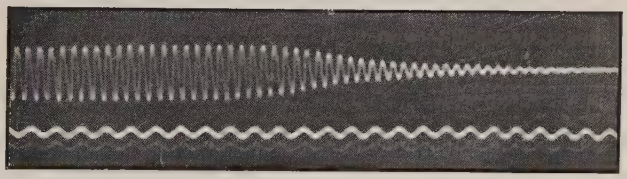


Fig. 11.

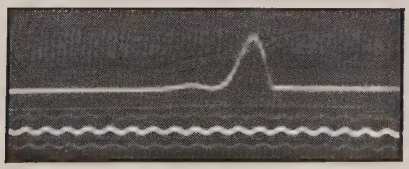
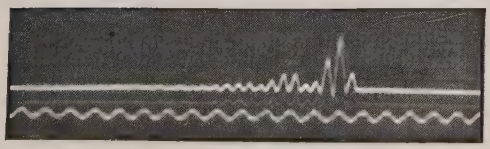


Fig. 15.



of the preceding oscillations was 753·6, and the capacity of the primary condenser 2·17 mfd. Consequently the value of $V_0$ in this experiment was

$$V_0 = \frac{1{\cdot}57\sqrt{2}\,.\,10^6}{2\pi\,.\,753{\cdot}6\,.\,2{\cdot}17}$$

$$= 216 \text{ volts.}$$

The calculated maximum secondary potential is therefore

$$V_{2m} = 140{\cdot}3 \times 216$$

$$= 30300 \text{ volts,}$$

which does not fall far short of the generally accepted value of 31000 volts required to spark across a 1 cm. gap of this kind.

It may be concluded that the method here adopted of substituting the observed damping coefficient $k_2$ of the quicker component, for the calculated value, in the expression for $V_2$ derived from the theory of the Tesla coil leads to a value for the maximum secondary potential at unshortcircuiting which agrees satisfactorily with experiment.

The effect of the valve in this experiment therefore appears to be, while leaving the damping of the slower component oscillation unaltered, to reduce considerably that of the more rapid component. In this way the valve raises the maximum secondary potential from $96{\cdot}4V_0$, the value which it would have if both oscillations were subject to their own natural damping, to $140{\cdot}3V_0$. The valve therefore serves the double purpose of first raising the primary condenser to a certain potential, and then increasing the ratio in which this potential is transformed in the secondary circuit.

The highest potential which it has been found possible to produce by the method of unshortcircuiting with the apparatus used in these experiments was 43000 volts. Probably much higher potentials can be attained by this method with more powerful valves.

Bangor, January 1924.

# LIX. *The Fluorescence of Æsculin Solutions.*

*By* Miss M. B. Kearney, *M.A.**

[Plate V.]

## 1. *Introduction.*

A CONSIDERABLE amount of work has been done recently on the fluorescence of organic solutions and the destruction of their fluorescent power by light. Perrin† has presented the view that the emission of fluorescence by organic substances is due to the flashes of exploded molecules: thus a molecule, having once emitted fluorescent light, has completely lost its power of fluorescence.

Wood ‡, working on the transformation of fluorescent solutions by concentrated sunlight, was unable to obtain satisfactory confirmation of Perrin's theory. He found that a solution of rhodamine could be transformed without the emission of fluorescence by maintaining it at a temperature of 100° C.

Pringsheim § carried out some experiments with fluorescein and eosin in various solvents and obtained results not capable of explanation by Perrin's hypothesis. He found that lowering of the temperature to −180° C., while retarding the photochemical action, had no influence on the intensity of the fluorescence. From theoretical considerations he regards Perrin's theory as unsatisfactory, since it places the fluorescence of organic solutions in a class separate from all analogous phenomena. He does not give any definite hypothesis as to the cause of fluorescence, but suggests that the molecules are excited by the absorption of light; from the excited state they either revert, with the emission of fluorescence, into the normal state or react chemically with other excited molecules and do not produce luminescence.

Kautsky and Zocher ‖ have made observations on the luminescence of unsaturated silicon compounds which are in agreement with Pringsheim's results, especially in regard to the dependence of the phenomenon on temperature.

* Communicated by Professor J. C. McLennan, F.R.S.
† J. Perrin, *Ann. de Phys.* (ix.), 10, pp. 133–159, Sept.-Oct. 1918.
‡ R. W. Wood, Phil. Mag. pp. 757–765, April 1922.
§ P. Pringsheim, *Zeits. f. Phys.* x. pp. 176–184 (1922).
‖ Kautsky and Zocher, *Zeits. f. Phys.* ix. pp. 267–284 (1922).

In a paper recently published by McLennan and Cale* are given the results of an investigation of the fluorescence of dilute aqueous solutions of æsculin. The interesting point is brought out that an aqueous solution of æsculin can be made to fluoresce for a long time without destruction of its fluorescence when excited by light of suitable wave-length.

In view of this work some further experiments have been made on the fluorescence of æsculin solutions, with the hope of extending our knowledge of the subject.

## 2. *Apparatus and Method.*

The method of transforming and testing solutions of æsculin was similar to that used by McLennan and Cale. Transformations were effected by exposure of the solutions to a quartz mercury arc lamp 35 cm. long and carrying about 5 amps. Two solutions were generally transformed simultaneously; these were placed symmetrically with respect to the lamp at a distance of 4 cm. from its axis.

A Nutting spectrophotometer was used to measure the intensity of the fluorescent light. The arrangement of the apparatus was as follows:—Light from a self-regulating carbon arc lamp, after passing through condensing lenses and a nickel oxide glass filter, was reflected downward by a mirror into two test-tubes, placed horizontally, which contained the fluorescent solutions. The fluorescent light passed through a slit and entered the openings of the photometer.

The width of the slit used throughout the course of the experiments was 5 mm. On account of the reflexion of light from the curved surfaces of the tubes containing the solutions, the fluorescent intensity of 5 mm. thickness of solution in the central portion of the tube was measured. The solutions were sufficiently dilute to show no noticeable absorption at this depth.

The standard solution was taken as 4 parts of æsculin to 100,000 parts of solvent by weight, and the intensity of the fluorescence emitted by a solution of strength 8/100,000,000 could be measured.

## 3. *Experiments with Ultraviolet Light.*

To verify the above-mentioned result of McLennan and Cale, aqueous solutions of æsculin, of strength 4/100,000, were sealed in two evacuated test-tubes, one of quartz and

* McLennan and Cale, Proc. Roy. Soc. London, A. cii. pp. 256–268 (1922).

one of glass. These were exposed to the light of a glass mercury arc-lamp for 20 hours, and measurements of the fluorescent intensity were taken every half-hour. A solution of the same concentration in a similar evacuated and sealed glass test-tube was used for comparison; this was compared with a freshly prepared solution four times during the experiment, and was found to have the same intensity every time. At the end of 20 hours neither solution which had been exposed showed any decrease in its fluorescent intensity.

This shows that none of the wave-lengths which are active in destroying the fluorescent power are transmitted by glass, whereas some, at least, of those causing fluorescence are in this region.

In a second experiment, solutions of æsculin in various solvents were exposed in evacuated and sealed quartz tubes to the light from a quartz mercury arc-lamp, and measurements were made of the fluorescent intensity at regular intervals during the exposure. The solvents used were water, ethyl alcohol, methyl alcohol, acetone, and glycerine; the initial concentration in every case was the same as that of the standard solution.

In sealing the quartz tubes after they were evacuated, precautions were taken to try to prevent ultraviolet light from the oxygen flame from penetrating the tubes and transforming the solutions. There was, however, sufficient light from the flame to cause a partial and easily measurable transformation, since, during the first few seconds of exposure, the rate of transformation is greatest. In order to obtain the initial portions of the decay curves solutions were exposed in corked quartz tubes.

Typical curves, showing the relation between intensity of fluorescence and length of exposure are shown in figs. 1 and 2.

Some characteristics of the curves noted are :—

(*a*) The initial fluorescent intensity was less for solutions in organic solvents than for aqueous solutions of the same concentration.

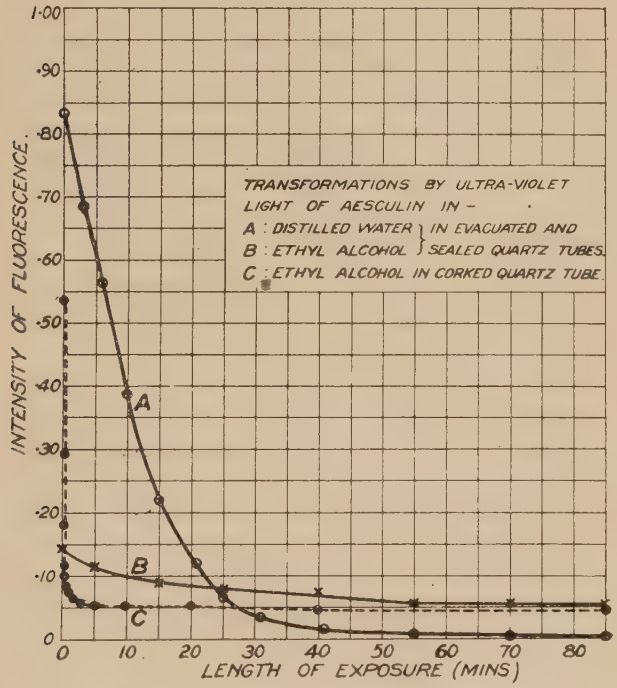
(*b*) For the first-mentioned solvents the initial portions of the decay curves showed a greater rate of transformation than that shown by the aqueous solution, whereas during the later part of the decay period the rate of transformation was less than that of an aqueous solution.

(*c*) Solutions in organic solvents required a much longer time of exposure to become completely transformed than those in water. A solution of æsculin in ethyl alcohol was

exposed for 18 hours before its fluorescence became too weak to be measured photometrically ; from fig. 1A it will be seen that the time of exposure for complete transformation of the same volume of aqueous solution was about 90 minutes.

(*d*) With the glycerine solution there appears to be a diffusion effect not noticed with any of the other solutions.

Fig. 1.



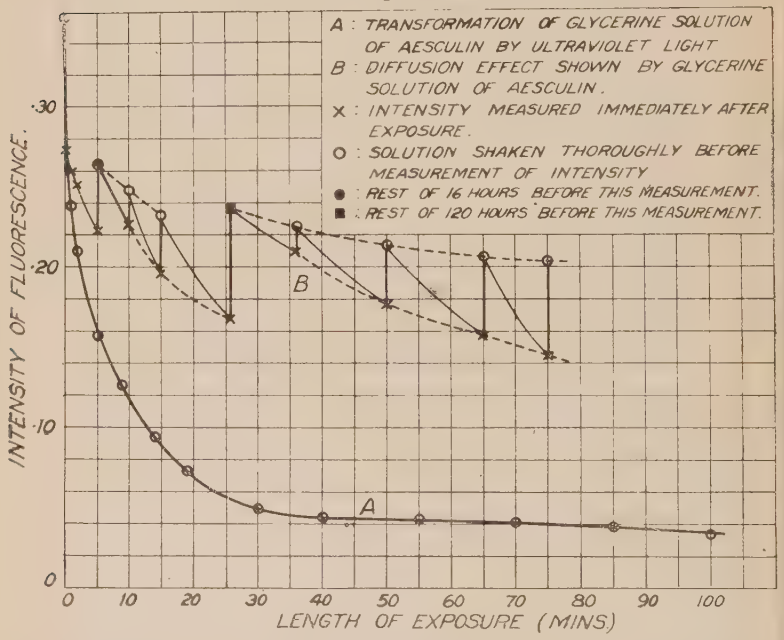

This is illustrated in fig. 2 B. After exposure for any period the intensity of fluorescence was found to depend on whether the solution had been shaken or not before being tested ; the same effect was obtained if the solution had been allowed to remain undisturbed for some time after exposure, and was probably due to the high coefficient of viscosity of glycerine.

### 4. *Experiments with Ozone.*

It has been noticed that aqueous solutions of æsculin are transformed by the passage of ozone through them, and that during the process of transformation an extremely faint bluish-white luminescence is emitted.

In order to obtain, if possible, a photograph of the spectrum of this glow, concentrated solutions of æsculin in water, acetone, glycerine, ethyl, methyl, and propyl alcohols were transformed by ozone. For every solution the intensity of the glow was extremely faint compared with the fluorescence of the solution under the action of ultraviolet light, so that

Fig. 2.


A : TRANSFORMATION OF GLYCERINE SOLUTION OF AESCULIN BY ULTRAVIOLET LIGHT
B : DIFFUSION EFFECT SHOWN BY GLYCERINE SOLUTION OF AESCULIN.
X : INTENSITY MEASURED IMMEDIATELY AFTER EXPOSURE.
O : SOLUTION SHAKEN THOROUGHLY BEFORE MEASUREMENT OF INTENSITY
● : REST OF 16 HOURS BEFORE THIS MEASUREMENT.
■ : REST OF 120 HOURS BEFORE THIS MEASUREMENT.
INTENSITY OF FLUORESCENCE.
·30
·20
·10
0
B
A
0 10 20 30 40 50 60 70 80 90 100
LENGTH OF EXPOSURE (MINS.)

all observations had to be made in a darkened room. The following table gives roughly the relative intensities of the glows, distilled water being taken as the standard solvent:—

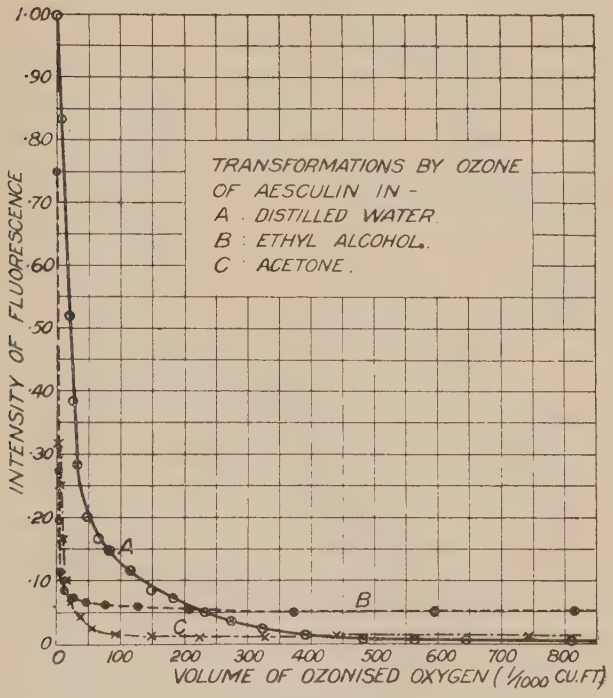
| Solvent. | Intensity of Glow. |
|---|---|
| Ethyl Alcohol | 5 |
| Propyl Alcohol | 5 |
| Methyl Alcohol | 3 |
| Acetone | 3 |
| Distilled Water | 1 |
| Glycerine | 0 |

The glow was brightest when ozone was first passed through a fresh solution, and decreased in intensity with further bubbling of ozone through it.

Ethyl alcohol was chosen as the most satisfactory solvent

with which to obtain the spectrum of the glow. A quartz tube was designed whereby a steady flow of fresh concentrated solution was maintained past an inlet for ozonized oxygen. A quartz spectrograph and a photographic plate most sensitive to blue light were used, but continued exposure for 9 hours produced nothing on the plate. As

Fig. 3.




the fluorescence spectrum was well brought out by a 20 minutes' exposure, the extreme faintness of the glow may be realized.

Photometric measurements were made of the fluorescent intensity of various solutions after the passage of known quantities of ozone through them. Fig. 3 shows the curves obtained for water, ethyl alcohol, and acetone. For the other solvents the curves are similar.

The intensity of the fluorescence of a glycerine solution was unaffected by the passage of ozone through it. Since no glow was produced in a glycerine solution, this would

seem to indicate that the glow is intimately associated with the decay of the fluorescent intensity. Another fact in support of this is that, during the initial rapid decay of the fluorescent intensity, the glow was brighter than it was when the rate of transformation had become small.

### 5. *Experiments with Æsculin Powder and at Low Temperature.*

It was thought that light might produce some effect on æsculin powder as well as on solutions. To test this, equal quantities (10 mgms.) of æsculin powder were spread evenly over the inner surfaces of evacuated quartz and glass tubes and were exposed to ultraviolet light for 50 hours. The tubes were then opened and the powder in each was dissolved in the same volume of distilled water. The fluorescent intensity of each solution was measured and showed no decrease with respect to the standard solution of the same concentration.

A similar experiment was performed with ozone. Through 10 mgms. of æsculin powder, 5 cubic feet of highly ozonized oxygen were passed. The solution prepared from this powder showed fluorescence equal to that of the standard solution.

This investigation was carried out with the view to experimenting at low temperatures, powder being more suitable than solutions for such work. The negative result prevented further work with powder, since the presence of a solvent is evidently necessary for the transformation of molecules of æsculin by ultraviolet light and ozone.

Since the freezing-point of pentane is below the temperature of liquid air, a solution of æsculin in pentane was prepared and its fluorescence was studied. At room temperature, it fluoresced weakly ; on lowering the temperature to that of liquid air, no change was observed in the intensity of the fluorescence. Pentane itself, however, showed fluorescence equal to that of the solution both at room and liquid-air temperatures.

### 6. *Absorption Spectra.*

Photographs of the absorption spectra of æsculin dissolved in glycerine and ethyl alcohol were obtained. Plate V. c and D show those obtained with glycerine solutions. The absorption spectra of fresh solutions of æsculin in glycerine

and ethyl alcohol had a band with maximum absorption at about $\lambda = 3400$A. This band was narrower and less intensely absorbed for the organic than for aqueous solutions. Since it is supposed that the emission of fluorescence is associated with this band, the less intense absorption of these wave-lengths may account for the less intense fluorescence emitted initially by organic solutions as compared with that of an aqueous solution.

In the absorption spectra of transformed glycerine and ethyl alcohol solutions, however, there was a band with a maximum at about $\lambda = 2700$A, which was not present in that of an aqueous solution.

Absorption spectra of solutions transformed by ultraviolet light were the same whether the transformation was effected in evacuated tubes or in contact with air. Solutions transformed with ozone have the same absorption spectra as those transformed by ultraviolet radiation.

### 7. *Protective Action of Transformed on Fresh Solutions.*

The absorption bands have been considered as indicating regions intimately related to the emission of fluorescence and the decay of the fluorescent intensity. In the absorption spectrum of an aqueous solution, it is supposed that the wave-lengths in both the bands are active in exciting fluorescence, and that those in the extreme ultraviolet band cause the decay of the fluorescent power as well.

If this be a correct interpretation, it would be expected that a fresh solution could be shielded from the radiation causing decay by surrounding it with a completely transformed solution which would absorb the wave-lengths in the ultraviolet band. To test this, a quartz tube containing a fresh aqueous solution of æsculin was suspended in a quartz flask filled with decayed solution. This system was exposed to ultraviolet light for six hours, tests of the fluorescent intensity being made every hour. Care was taken to prevent any portion of the tube, except that containing the solution, from being exposed. It was found that the fluorescence was just as intense after exposure as it was initially. During the exposure, the solution fluoresced brilliantly, due to the transmission of wave-lengths in the upper band.

To make certain that this result was not due merely to the decreased intensity of the light after passing through a considerable thickness of solution, distilled water was

substituted for the decayed solution and the experiment was repeated. At the end of an hour, the fluorescent intensity had decreased noticeably and, after five hours' exposure, it had fallen to about one-fourth its original value.

Some further work should be done on the protective action of glycerine and alcoholic solutions to ascertain whether the presence of the band at $\lambda = 2700$A causes any change in the shielding effect.

## 8. *Summary.*

1. The initial fluorescent intensity of a solution depends on the solvent used ; it is greater for aqueous solutions than for organic solutions of the same concentration.

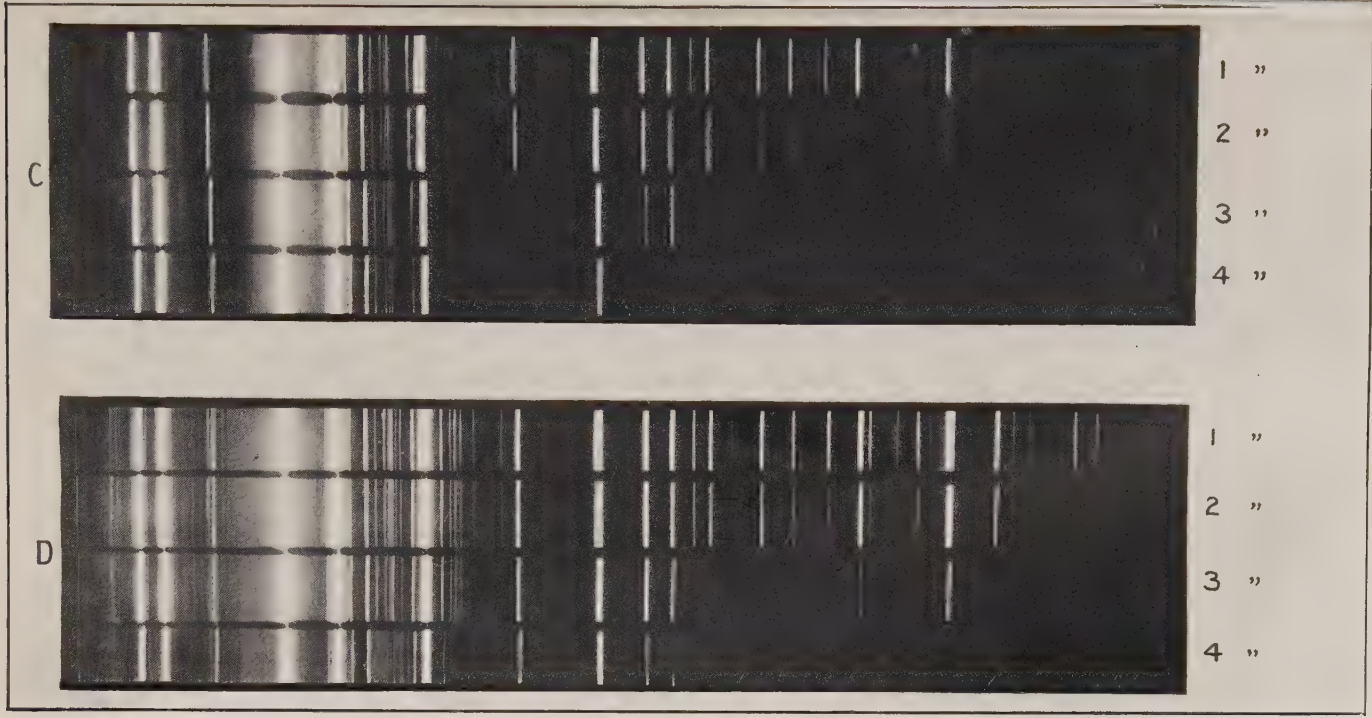
2. For solutions of equal concentration, the initial rate of transformation by ultraviolet light and ozone is greater for organic than for aqueous solutions, but organic solutions require a much longer exposure for complete transformation.

3. The presence of a solvent is essential for the transformation of æsculin ; ultraviolet light and ozone produce no change in æsculin powder.

4. It has been verified that a solution can be made to fluoresce without being destroyed by exposing it either in an evacuated glass tube, or in a quartz tube surrounded by a transformed solution. In both cases, the extreme ultraviolet wave-lengths are cut off, showing that the decay of the fluorescent intensity is due to the wave-lengths in the extreme ultraviolet region.

In conclusion, the writer wishes to express her sincere thanks to Professor J. C. McLennan for suggesting the problem and for his kindly interest, also to Mr. J. F. T. Young for his helpful suggestions. Thanks are due to the Honorary Advisory Council for Scientific and Industrial Research of Canada for the award of a Bursary by which the writer was enabled to carry out the investigation.

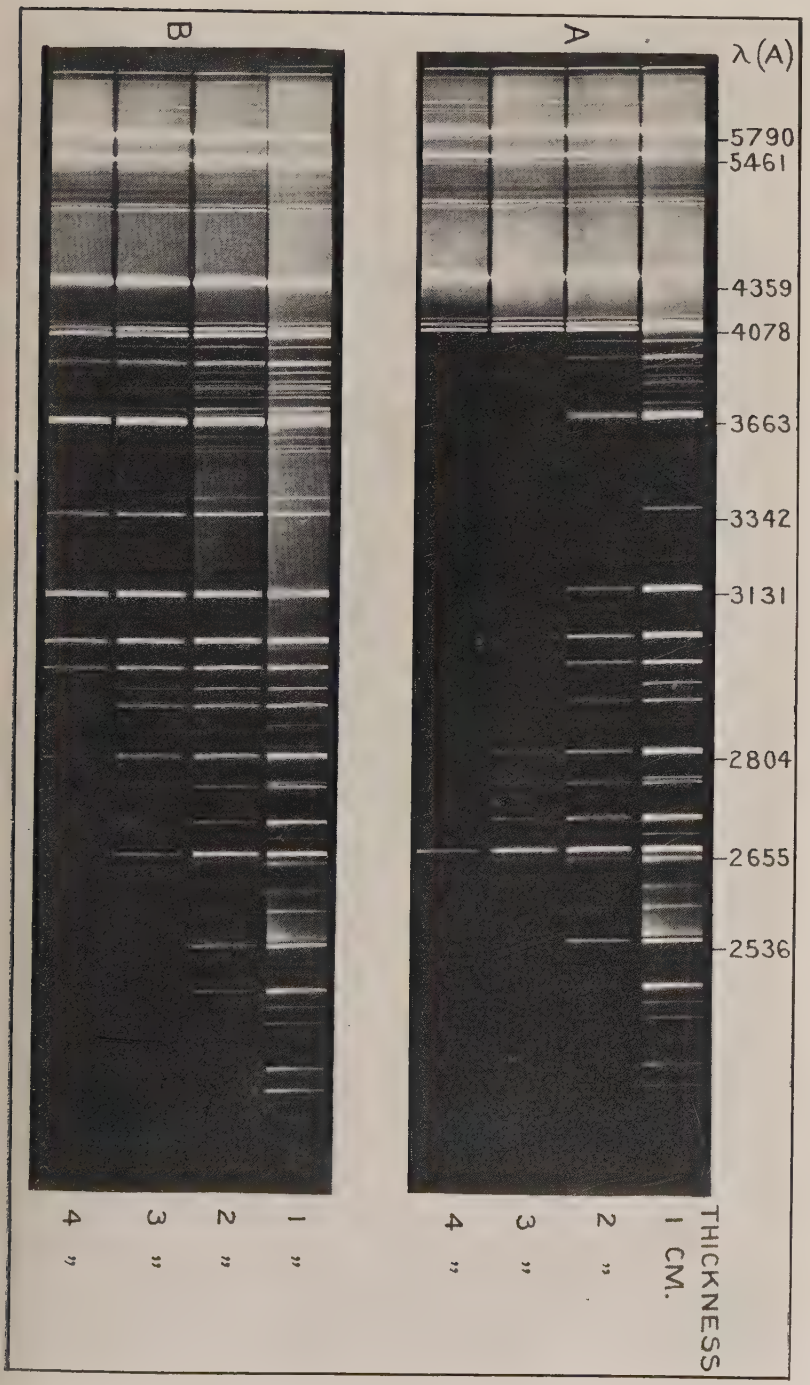
The Physical Laboratory,
University of Toronto.
May 30th, 1923.




M. B. Kearney.

Absorption Spectra of Æsculin Solutions.

A. Aqueous solution unexposed.
B. „ „ decayed.
C. Glycerine „ unexposed.
D. „ „ decayed.


A
B
λ(A)
5790
5461
4359
4078
3663
3342
3131
2804
2655
2536
THICKNESS
1 CM.
2 "
3 "
4 "
1 "
2 "
3 "
4 "

LX. *The Crystal Structure of Metallic Arsenic.* *By* A. J. Bradley, *M.Sc., Research Student in Physics, The Physical Laboratories, The University, Manchester* *.

## 1. *Introductory.*

THE metallic form of arsenic is described by Groth †. It has a density of 5·727 (Bettendorf) or 5·71 (Petersen). It crystallizes in greyish crystals possessing the symmetry of the ditrigonal scalenohedral class (dihexagonal alternating) of the rhombohedral system. If the crystal be referred to hexagonal axes the axial ratio $a:c$ is 1 : 1·4025 (G. Rose). In this paper the three edges of the unit rhombohedron which meet in the trigonal axis will be taken as crystallographic axes. The angle $\theta$ (100) : (010) $= 94° 56'$ (G. Rose). This corresponds to an angle $\gamma = 84° 36'$ between the three axes, though by an arithmetical error Groth gives 85° 38′. The crystals when obtained by sublimation often twin parallel to the (110) face. Cleavage occurs most readily parallel to the (111) face, but it may also occur parallel to the (110) face.

Crystals of arsenic of this type are isomorphous with the corresponding crystals of antimony and bismuth. The structure of the former has been determined by R. W. James and N. Tunstall ‡, and that of the latter by R. W. James §. The structures of both antimony and bismuth follow the same pattern, and from its resemblance to the other two elements arsenic was expected to have the same type of structure.

## 2. *Experimental Methods.*

The method adopted was that of the powder photograph. A Shearer X-ray tube with a copper anticathode was used, and the radiation so obtained was filtered through nickel foil. In this way a homogeneous beam of $K_\alpha$ copper radiation of wave-length $1·539 \times 10^{-8}$ cm. was directed into the camera. This was cylindrical in shape with its axis vertical and its diameter was about one inch. The finely-powdered arsenic was made into a paste with fish-glue and

* Communicated by Prof. W. L. Bragg, F.R.S.
† *Chemische Kristallographie*, i. Teil 19.
‡ Phil. Mag. xl. p. 233 (1920).
§ Phil. Mag. xlii. p. 193 (1921).

mounted on a hair placed vertically at the centre of the camera. The thickness of the powder was about ·1 mm. The beam of X-rays diverging from a gold slit about ·1 mm. wide entirely surrounded the powder. The film was fastened round the circumference of the camera by rubber bands and was exposed to the radiation for about 45 minutes, the tube being run at 9 milliamperes and 30000 volts.

The film was measured by a travelling microscope and the figures so obtained are shown in Table I., Column I. $s$ = distance measured on film between corresponding lines. These lines require to be corrected for a slight eccentricity in the position of the hair. The centre of the stick of powder was ·2 mm. behind the axis of the camera, and therefore further away from the film than it should have been. This makes the measured values of $s$ too great, the error being in each case $+(\cdot 40 \sin 2\theta)$ mm., where $\theta$ is the glancing angle of incidence. The corrected values for $s$ are given in Column II. The diameter of the camera was 2·55 cm. This must be corrected for the thickness of the film. The film used in these experiments was sensitized on both sides and was ·20 mm. thick. On wrapping the film round the camera, one side is stretched and the other contracts. The celluloid is sufficiently elastic to flatten out again after development. It has been assumed that the amount of contraction on the inner side is exactly equal to the expansion on the outer side. This is equivalent to assuming that the length of the centre of the film is invariable. The effective radius of the camera was taken as the distance from the centre of the powder to the centre of the film, and was ·10 mm. more than the actual radius. The effective diameter D was therefore 2·57 cm.

$\theta$ the glancing angle of incidence is given by

$$\theta = \frac{s}{4\pi \mathrm{D}} \times 360^\circ = 1\cdot 111\, s^\circ.$$

In Column V.,

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta} = \frac{\cdot 7695}{\sin \theta} \text{ Å},$$

where $d$ is the spacing of the atomic planes and $n$ is the order of reflexion. $\lambda = 1\cdot 539$ Å is the wave-length of the radiation.

The factors used in these calculations were checked from a photograph of rock-salt which gave a mean value of 5·633 Å for the side of a unit cube. The standard value is 5·628 Å. The difference is less than 1 in 1000.

### 3. *General Form of Arsenic Structure.*

The structure of antimony and bismuth can best be visualized as two interpenetrating face-centred rhombohedral lattices related to one another in almost the same way as the sodium and chlorine lattices in rock-salt. The lattices regarded in this way are almost cubic, but are however slightly elongated parallel to a trigonal axis, and one lattice is slightly displaced with respect to the other in a direction parallel to the trigonal axis. The spectra observed in the case of arsenic admit of a similar explanation.

If the atoms of arsenic were arranged at the corners of a rhombohedron so that they lay on a simple rhombohedral lattice, we should have the simplest possible arrangement compatible with the crystallographic data. The unit cell would contain one atom of arsenic. From the data of Groth it is possible to calculate the length of side of a unit rhomb of this type. Taking the density of arsenic as 5·72, the length of side $a = 2{\cdot}805$ Å. From $a$ and $\gamma$ all possible values of $\frac{d}{n}$ down to ·850 A were calculated. Reflexions were found corresponding to almost all these values, but in addition there were lines on the film corresponding to twice the normal spacings in the case of odd planes such as (111), (311). This is the type of spectra peculiar to a face-centred structure, the length of side of a unit rhomb being $2a$ and each rhomb containing four atoms. The value obtained for $a$ shows there are eight atoms of arsenic to each unit cell. The structure must consist of two interpenetrating face-centred rhombohedral lattices. All values of $\frac{d}{n}$ for such a system were calculated and compared with the observed values in Column V. They were found to be on an average 0·2 per cent. higher than the experimental values. The calculated values are given in Column VI., after allowing for this difference. The density as determined from X-ray data is 5·75, $a = 2{\cdot}799$.

TABLE I.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|---|---|
| | $s$ mm. | $s$ (corrected) mm. | $\theta$. | $\sin\theta$. | $\frac{d}{n}$ (Obs.) $\times 10^{-8}$ cm. | $\frac{d}{n}$ (Calc.) $\times 10^{-8}$ cm. | $hkl$. | Order of Intensity Obs. | Order of Intensity Calc. | Error. |
| 1 | 11·41 | 11·24 | 12·50 | ·2164 | 3·555 | 3·529 | 111 | 19 | 19 | ... |
| 2 | 12·8 | 12·6 | 14·0 | ·242 | 3·18 | 3·118 | $1\bar{1}1$ | 25 | 24 | 1 |
| 3 | 14·65 | 14·44 | 16·05 | ·2765 | 2·780 | 2·777 | 200 | 1 | 1 | ... |
| 4 | 20·07 | 19·79 | 22·01 | ·3749 | 2·054 | 2·054 | 220 | 3 | 3 | ... |
| 5 | 21·92 | 21·62 | 24·03 | ·4070 | 1·891 | 1·886 | $2\bar{2}0$ | 2 | 2 | ... |
| 6 | 23·29 | 22·98 | 25·56 | ·4316 | 1·781 | 1·790 | 311 | 4 | 9 | 5 |
| 7 | 23·55 | 23·24 | 25·83 | ·4358 | 1·764 | 1·764 | 222 | | | |
| 8 | 25·13 | 24 80 | 27·57 | ·4628 | 1·662 | 1·662 | $3\bar{1}1$ | 12 | 15 | 3 |
| | | | | | | 1 614 | $\bar{3}11$ | ... | 26 | ... |
| 9 | 26·83 | 26·49 | 29·46 | ·4919 | 1·562 | 1·559 | $2\bar{2}2$ | 8 | 7 | 1 |
| 10 | 30·66 | 30·29 | 33·68 | ·5545 | 1·387 | 1·388 | 400 | 5 | 4 | 1 |
| 11 | 31·15 | 30·78 | 34·22 | ·5624 | 1·368 | 1·368 | 331 | | | |
| 12 | 33·44 | 33·06 | 36·78 | ·5988 | 1·286 | 1·291 | $33\bar{1}$ | 7 | 8 | 1 |
| | | | | | | 1·287 | 420 | | | |
| 13 | 35·42 | 35·03 | 38·95 | ·6286 | 1·223 | 1·227 | 422 | 23 | 23 | ... |
| | | | | | | 1·226 | $3\bar{3}1$ | | | |
| 14 | 36·18 | 35·78 | 39·80 | ·6401 | 1·201 | 1·201 | $4\bar{2}0$ | 6 | 5 | 1 |
| 15 | 36·85 | 36·45 | 40·55 | ·6501 | 1·182 | 1·177 | 333 | 21 | 21 | ... |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 39·45 | 39·05 | 43·45 | ·6877 | 1·119 | 1·119 | 422 | 9 | 6 | 3 |
| 17 | 39·97 | 39·57 | 44·00 | ·6947 | 1·107 | 1·109 | 511 | | | |
| 18 | 40·82 | 40·42 | 44·95 | ·7065 | 1·089 | 1·088 | $\bar{4}22$ | 14 | 14 | ... |
| 19 | 41·96 | 41·56 | 46·15 | ·7211 | 1·068 | 1·066 | $5\bar{1}1$ | 15 | 15 | ... |
| 20 | 43·27 | 42·87 | 47·65 | ·7390 | 1·041 | 1·039 | $3\bar{3}3$ | 20 | 22 | 2 |
| | | | | | | 1·038 | $\bar{5}11$ | | | |
| 21 | 44·27 | 43·87 | 48·75 | ·7516 | 1·023 | 1·027 | 440 | 24 | 25 | 1 |
| | | | | | | 1·005 | 442 | ... | 28 | ... |
| 22 | 45·82 | 45·43 | 50·50 | ·7716 | ·998 | ·997 | 531 | 10 | 10 | ... |
| 23 | 48·74 | 48·36 | 53·75 | ·8065 | ·955 | ·955 | 531 | 16 | 13 | 3 |
| 24 | 49·65 | 49·27 | 54·75 | ·8166 | ·942 | ·943 | 440 | 18 | 18 | ... |
| 25 | 50·78 | 50·41 | 56·00 | ·8290 | ·929 | ·9265 | 600 | 11 | 11 | ... |
| | | | | | | ·9265 | 442 | | | |
| 26 | 51·30 | 50·94 | 56·60 | ·8348 | ·922 | ·9215 | 533 | | | |
| 27 | 52·34 | 51·99 | 57·85 | ·8466 | ·908 | ·910 | $5\bar{3}1$ | 22 | 20 | 2 |
| | | | | | | ·902 | 620 | | | |
| | | | | | | ·902 | $\bar{5}31$ | | | |
| 28 | 54·00 | 53·65 | 59·70 | ·8634 | ·891 | ·895 | 622 | 13 | 12 | 1 |
| | | | | | | ·892 | 442 | | | |
| | | | | | | ·882 | 444 | ... | 27 | ... |
| 29 | 58·12 | 57·81 | 64·30 | ·9011 | ·854 | ·856 | $6\bar{2}0$ | 17 | 17 | ... |
| | | | | | | | | Total Error ..... | | 25 |

The agreement between Columns V. and VI. proves the nature of the space lattices of which the arsenic structure is built up, but throws no light on their mutual relationship. That they can only be displaced from a position of coincidence by a movement along the trigonal axis follows from considerations of symmetry. The most symmetrical arrangement would make the displacement exactly one-half of the length of the diagonal of the rhombohedral cell containing eight atoms of arsenic. This arrangement constitutes the simple rhombohedral structure which has already been shown to be impossible, since the spacing of planes with odd indices is doubled. The amount of displacement from this simple arrangement can only be determined from a consideration of the relative intensities of reflexion from the various planes of the crystal.

The intensity of reflexion from one lattice of arsenic only can be calculated as follows. For this purpose we must assume the validity of some empirical expression which will give the total intensity of reflexion for any one set of planes. In the case of rock-salt, W. H. Bragg* found that the intensity of reflexion falls off approximately with the square of the sine of the glancing angle, this relation including the progressive decrease in intensity of reflexion from each atom due to the distribution of its electrons. The intensity is further reduced by the effects of thermal agitation, but these only come into play in the case of very closely spaced planes. If we assume that the same law holds for arsenic and that the effect of thermal agitation in reducing the reflexion at large angles is negligible, we obtain the following expression for the intensity of reflexion from any plane $(hkl)$ reflecting radiation at an angle $\theta$:

$$I = \frac{NA}{\sin^2 \theta},$$

where A is a constant, being a function of the scattering power of arsenic, and N is the number of faces corresponding to the form $\{hkl\}$.

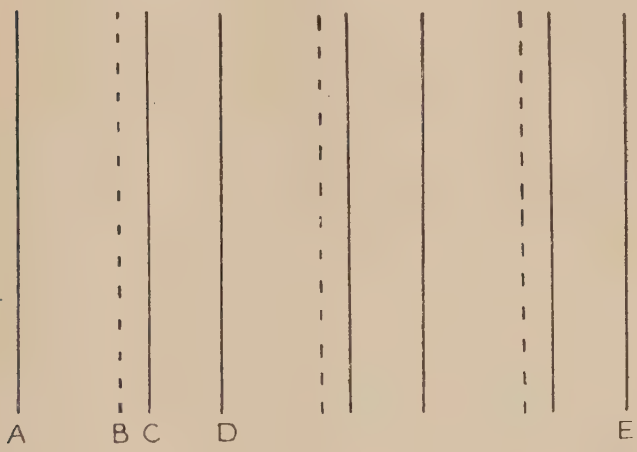
To obtain the combined effect of the two lattices allowance must be made for the phase difference between reflexions from atoms of different lattices. This phase difference is not the same for different planes, but it can easily be calculated for each case.

The arrangement of atoms in the 111 planes is represented in fig. 1. If the atoms were arranged on a simple rhombo-

* W. H. Bragg, Phil. Mag. xxvii. p. 881 (May 1914).

hedral lattice the spacing would be AB. The displacement of the plane of atoms from B to C doubles the spacing, which is now AD ($d_{111}$). There are three repetitions of AD as we pass along the diagonal of a unit cell from A to E, so that AE=3AD. Let the ratio of BC to AE be $x$. Then BC=3$x$ . AD=3$xd_{111}$.

Fig. 1.



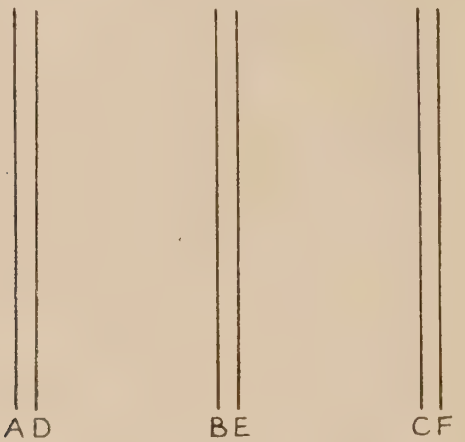

The phase difference between A and D is $2n\pi$ for a $n$th order reflexion. The phase difference between A and C will be $2n\pi(\frac{1}{2}+3x)$. As $x$ increases, up to a certain limit the pairs of planes will approach closer together. If $n$ is odd, the phase difference increases from an odd number of half-wave lengths to an even number, and the intensity of reflexion increases. If $n$ is even the reverse is the case, and the intensity falls off.

The arrangement of atoms in the 100 planes is shown in fig. 2. Only half the atoms in each plane of the simple structure are displaced. The displacement of half the atoms in plane A to D does not affect the unit spacing of the planes. The spacing between opposite faces of the unit cell ($d_{100}$) is now AC, but there is no reflexion corresponding to this distance. The first reflexion will correspond to the spacing AB($d_{200}$). As before, the distance AD=$x$AC=$xd_{(100)}$. The phase difference between A and C is $2n\pi$ for a $n$th order reflexion, but as B is exactly half way between A and C there will only be even order reflexions. The phase difference between A and D is $2n\pi x$. In this case, as $x$ increases the

phase difference increases and the intensity lessens until it ultimately falls to zero.

All planes belong to either Class I. (Planes like (111)) or Class II. (Planes like (100)). The general formula for any

Fig. 2.




plane $hkl$ can be obtained as follows. Taking the crystallographic axes as Cartesian axes, the positions of the atoms composing the structure may be represented thus :—

| | |
|---|---|
| $m, n, p$ | $m+x+\frac{1}{2}, n+x+\frac{1}{2}, p+x+\frac{1}{2}$ |
| $m+\frac{1}{2}, n+\frac{1}{2}, p$ | $m+x+1, n+x+1, p+x+\frac{1}{2}$ |
| $m, n+\frac{1}{2}, p+\frac{1}{2}$ | $m+x+\frac{1}{2}, n+x+1, p+x+1$ |
| $m+\frac{1}{2}, n, p+\frac{1}{2}$ | $m+x+1, n+x+\frac{1}{2}, p+x+1$ |

where $m$, $n$, $p$ are integers and $x$ is the displacement of the second lattice from the simple rhombohedron, as a fraction of the length of the long diagonal of the unit rhombohedron, which contains eight atoms of arsenic.

If $x_1y_1z_1$ be any point on the second lattice, its distance $d$ from a plane $hkl$ of the first lattice which passes through the origin is given by

$$d=(hx_1+ky_1+lz_1)d_{(hkl)},$$

where $d_{(hkl)}$ is the distance between planes $(hkl)$ passing through the atoms $m, n, p$ ; $m+1, n+1, p+1$, etc.

The distance between corresponding planes of the two lattices will therefore be

$$\begin{aligned} d&=(h(x+\tfrac{1}{2})+k(x+\tfrac{1}{2})+l(x+\tfrac{1}{2}))d_{hkl} \\ &=(x+\tfrac{1}{2})(h+k+l)d_{hkl}. \end{aligned}$$

If $x_2y_2z_2$ be any point on the first lattice, its distance $d$ from any plane $hkl$ of the same lattice passing through the origin is given by

$$d' = (hx_2 + ky_2 + lz_2)d_{hkl},$$

where $d_{hkl}$ has the same meaning as before.

By giving $x_2y_2z_2$ different integral values we find that the distance between neighbouring planes $d_1$ is given by $d_1 = d_{hkl}$ for planes with odd indices (111, 311), $d_1 = \frac{1}{2}d_{hkl}$ for planes with mixed indices (100, 210). If there is a phase difference $2r\pi$ between waves reflected from neighbouring planes of the same lattice, $r$ being an integer, reflexion will occur. Thus in the case of planes with mixed indices, $d_{hkl}$ represents a phase difference $4r\pi$ and only even order reflexions will occur. With this proviso $d_{hkl}$ always represents a phase difference $2n\pi$, where $n$ is an integer representing the order of reflexion.

The spacing $d$ will therefore represent a phase-lag $(x+\frac{1}{2})(h+k+l)2n\pi$. If we adopt the usual convention and incorporate the factor $n$ in the indices $hkl$ as has been done in Column VII., the phase-lag becomes $(x+\frac{1}{2})(h+k+l)2\pi$. This expression gives the phase difference between waves reflected from corresponding planes of different lattices. The amplitudes of the two waves are equal, so the total effect will be proportional to

$$[2 + 2\cos(x+\tfrac{1}{2})(h+k+l)2\pi].$$

The total intensity of reflexion I will be given by

$$\mathrm{I} = \frac{\mathrm{NA}}{\sin^2\theta}[2 + 2\cos(x+\tfrac{1}{2})(h+k+l)2\pi]. \quad . \quad . \quad (1)$$

The constant A can be omitted for comparative purposes. From this expression I was calculated for different planes and for various values of $x$ from 0 to ·075.

### 4. *Evaluation of the Indeterminate Parameter* x.

From equation (1) it follows that if $x=0$, the phase factor is zero if $(h+k+l)$ is odd and is equal to 4 if $(h+k+l)$ is even. These are minimum and maximum values respectively, and as $x$ increases the values will change periodically.

For every value of $x$ between 0 and ·5 there is a different series of values for I, and in order to fix the most probable value of $x$ it is only necessary to find the best agreement

between the observed intensities of reflexion and the calculated values of I. It is impossible to get absolute values of intensity by the photographic method, and comparative quantitative estimates of blackening are not easy to get photometrically, partly because of the difficulty of allowing for the background of general radiation, and also because of the varying widths of the lines and the feebleness of some of them. It is, however, much easier to arrange the lines in order of intensity of blackening. The intensity of blackening was estimated by viewing the film through a low-power microscope illuminated from below so that the lines showed up as much as possible. The line that appeared darkest in comparison with its background after allowing for its width was marked 1. The next darkest was marked 2 and so on. The results of this comparison are shown in Column VIII.

In order to test the validity of this method a comparison of the intensities of reflexion from rock-salt was made in this way. Assuming the law of the square of the cosecant to hold, we get in the case of rock-salt

$$I = \frac{N(F_{Na}+F_{Cl})^2}{\sin^2\theta} \quad \text{for planes with even indices,}$$

$$I = \frac{N(F_{Na}-F_{Cl})^2}{\sin^2\theta} \quad \text{for planes with odd indices,}$$

where I, N have the same meanings as before, and $F_{Na}$, $F_{Cl}$ are proportional to the number of electrons in the ions of sodium and chlorine respectively. On comparing the intensities of reflexion so calculated with those obtained experimentally for the first twelve lines, it was found that they fell off in precisely the same order.

In the case of arsenic the intensities depend on the parameter $x$ which may assume any value between certain limits. In order to guide us to an approximate value of $x$ we must consider the peculiarities of one or two lines on the film. Lines 311, 442 and 444 entirely disappear. For the first line $h+k+l=1$, and the intensity of reflexion will be low for fairly small values of $x$, but not for medium or high values. Comparing this with 111 we again find a small reflexion showing $x$ to be small. The lines 442, 444 disappear for

$$x = \frac{2n+1}{2} \frac{1}{h+k+l},$$

where $n$ is an integer.

The smallest values giving zero reflexions are $x=\cdot05$ and $x=\cdot15$ for 442, and $x=\cdot0417$ and $x=\cdot125$ for 444. The line 200 is by far the brightest on the film. $x$ must therefore be much less than ·25, for which value the 200 reflexion disappears. The line 220 is the third strongest. It would disappear for $x=\cdot125$ or ·375. $x$ must therefore be considerably less than ·125. A value in the neighbourhood of $x=\cdot04$ or $x=\cdot05$ will fit in with all these facts.

Values of I were calculated for various values of $x$ in the neighbourhood of ·05, and for each value of $x$ a table was arranged giving the intensities in descending order of magnitude. Column IX. shows the order for $x=\cdot0488$. In the last column are given the difference between the calculated and observed orders in the case of each line. The arithmetic sum of these differences is 25. If $x$ be given other values the divergency between observed and calculated values rapidly increases. This is shown in Table II., where the total difference between observed and calculated orders of intensity is given for various values of $x$.

TABLE II.

| Displacement ($x$) ... | ·025 | ·04 | ·0425 | ·045 | ·046 | ·0475 | ·049 | ·0495 | ·05 | ·055 | ·06 | ·075 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total error in Order of Intensity... | 96 | 44 | 40 | 32 | 32 | 27 | 25 | 27 | 31 | 38 | 52 | 100 |

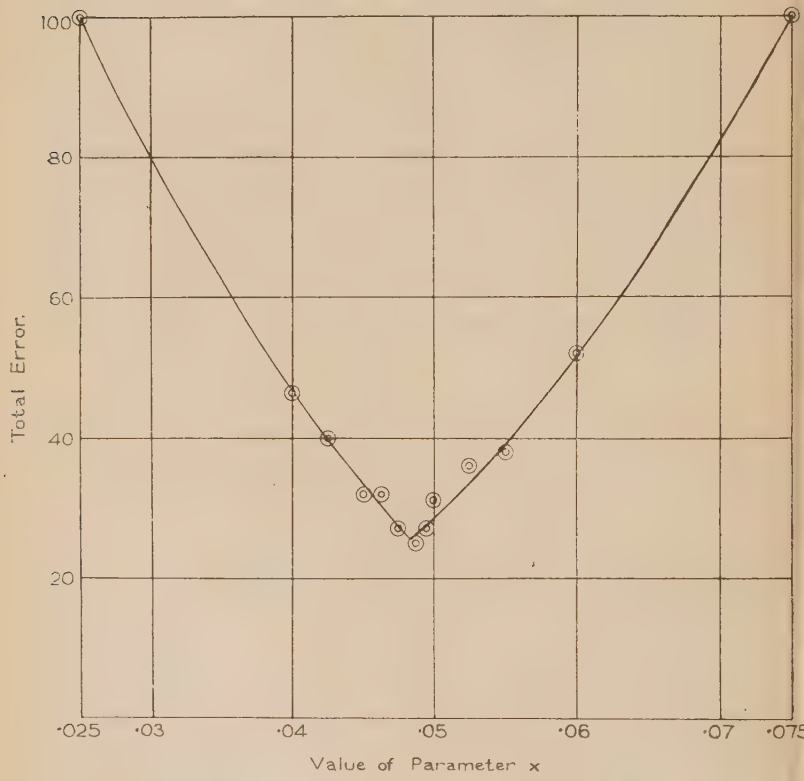
The data of Table II. are shown graphically in fig. 3. There is a very well marked minimum of error in the region $x=\cdot0485$. This may therefore be taken as the most probable value of $x$.

James and Tunstall * expressed the value of the parameter as a fraction of the length of the diagonal of a rhombohedron containing only one atom of antimony or bismuth. In order to compare the value here obtained for arsenic with those found for the other two metals it must therefore be doubled. We then have the value $x=\cdot097$ as the ratio of displacement to length of diagonal of unit rhomb containing one atom of arsenic. The result is almost independent of the validity of the empirical law connecting the intensity with the sine of the glancing angle. This is true because those lines which increase or decrease in intensity with increase of $x$ are scattered over the film quite promiscuously. The substitution of another empirical law will therefore scarcely alter that value of $x$ which gives the best agreement between observed

* *Loc. cit.*

and calculated orders of intensity, but will merely decrease or increase the total error for every value of $x$ alike. Actually, as the close agreement between Columns VIII. and IX. shows, the empirical law is very nearly true.

Fig. 3.




### 5. *Comparison of Arsenic, Antimony, and Bismuth.*

Each atom of arsenic has six nearest neighbours, three at a distance of $2{\cdot}51 \times 10^{-8}$ cm. and three at $3{\cdot}15 \times 10^{-8}$ cm. The three nearest lie in a plane (111) perpendicular to the trigonal axis and close to the parallel plane containing the first atom. The other three also lie in a plane perpendicular to the trigonal axis, but on the other side of the first atom and much farther away. In this way the whole structure is divided into double sets of planes separated by quite wide gaps from the next set. Cleavage naturally occurs

parallel to these planes (111). Table III. compares this and other properties in the case of the three elements.

TABLE III.

| | As. | Sb. | Bi. |
|---|---|---|---|
| Edge of Unit Rhomb $2a$ ... | 5·60 Å | 6·20 Å | 6·56 Å |
| Parameter $2x$ ... | ·097 | ·074 | ·052 |
| Longer Atomic Distance ... | 3·15 Å | 3·37 Å | 3·47 Å |
| Shorter „ „ ... | 2·51 Å | 2·87 Å | 3·11 Å |

The structure of arsenic, like that of antimony and bismuth, is a Sohncke point system. The two face-centred lattices of which it is composed are actually simple rhombohedral lattices of axial ratio 2·805 and length of edge of rhomb $4{\cdot}145 \times 10^{-8}$ cm. The structure is thus a special case of Sohncke's Point System No. 22—Das Zusammengesetzte Rhomboëdersystem. This simplifies to a system of point-pairs *, in which each point is at the centre of gravity of three of the original points. The two points of each pair are vertically above one another and are separated by a fraction $\frac{1}{2}+x$ of the distance between successive pairs.

In fig. 4 the plain circles represent atoms lying on a single lattice. If this be regarded as a face-centred lattice the rhombohedron ABCDEF is the unit. In this case AB = 5·60Å. There are four atoms of the first lattice to each unit rhomb and four of the second lattice (represented by shaded circles). The smaller and more acute rhombohedron AGHDJK is the unit cell of the structure regarding it as composed of two simple rhombohedral lattices. It contains only one atom of each lattice. AG = 4·145 Å. The points LMNS of the second lattice correspond to the points AGKR of the first, and A and L constitute a point pair.

*Summary.*

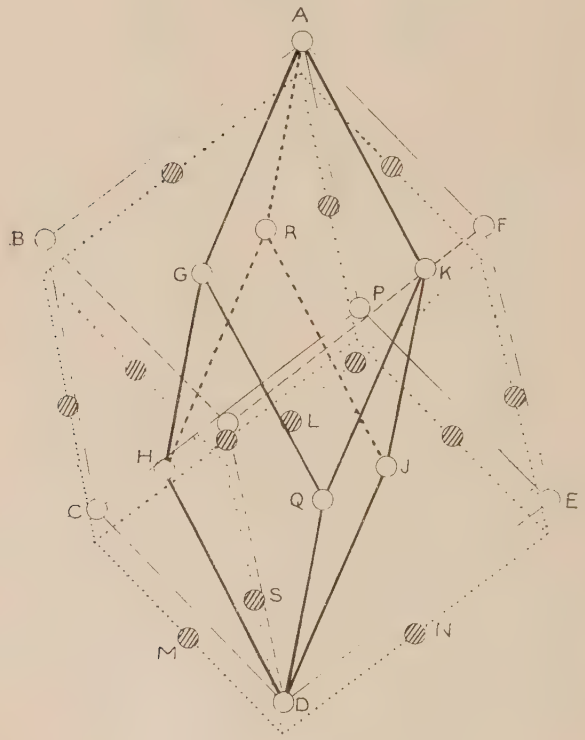
The structure of metallic arsenic was found by the analysis of an X-ray spectrograph of the powdered material. The general form of the structure was the same as that of antimony and bismuth which had already been elucidated.

Measurements of the film agreed well with calculations made from the crystallographic data. The structure consists of two interpenetrating rhombohedral space lattices which

* Sohncke, *Entwickelung einer Theorie der Kristallstruktur*, 1871, p. 131.

together form a Sohncke point-system. In order to find the relationship between the two lattices it was necessary to evaluate the parameter $x$ which fixes their relative position. For this purpose a comparison was made of the relative intensities of all lines on the film, and these were arranged

Fig. 4.




in descending order of intensity. The intensity of reflexion at any reflecting angle was calculated from a general formula for various values of $x$, and for each value the reflexions were arranged in order of intensity. On comparing these orders with that actually observed, one value of $x$ was chosen as giving the best agreement. This parameter was found to be greater than for either antimony or bismuth. Finally, several properties of the three elements were tabulated. In all cases antimony was found to be intermediate in character between arsenic and bismuth.

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## LXI. *On the Mean Distance between neighbouring Molecules in a Fluid.* *By* C. V. Raman*.

### 1. *Introduction.*

In connexion with the theory of the scattering of X-rays in fluids developed by the author and Dr. Ramanathan in a recent paper †, it was found that the evaluation of the results required a knowledge of the mean distance between neighbouring molecules in a fluid. On reviewing the literature of molecular theory, it was found that the problem of finding this distance had been attempted, but not in an entirely adequate or satisfactory manner ‡. It is proposed, in this paper, to consider the question and it will be found that the discussion raises some points of interest in relation to the kinetic theory of fluids.

### 2. *Ideal Gases.*

The theory of dimensions suggests that the mean distance $\lambda$ between neighbouring molecules could be expressed in terms of the number $n$ of the molecules per unit volume of the fluid by a formula of the type $kn^{-1/3}=\lambda$, where $k$ is a pure number. If we could postulate that the molecular centres occupy the corners of a cubical space-lattice, then obviously $k=1$. Actually, however, in a fluid, the arrangements of the molecules cannot be so definite, and $k$ must,

* Communicated by the Author.

† Proceedings of the Indian Assn. for the Cultvn. of Science, vol. viii. part 2 (1923).

‡ P. Hertz, *Math. Annalen*, lxvii. p. 387 (1909); R. Gans, *Physikalische Zeitschrift*, xxiii. p. 109 (1922).

therefore, in general, differ from unity. For the case of an *ideal* gas, in which the distribution of the molecules is absolutely chaotic, $\lambda$ may be evaluated in a perfectly rigorous manner. Consider any specified molecule A, and denote by $P(r)\,dr$ the probability that the nearest neighbour of A lies at a distance between $r$ and $r+dr$ from it. Then the mean distance $\lambda$ between A and its nearest neighbour is obtained by averaging, thus :—

$$\lambda=\int_0^\infty r\,P(r)\,dr. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$P(r)\,dr$ may be evaluated very simply by the use of Boltzmann's principle. The work W required to evacuate a spherical volume of radius $r$ is $pdv=4/3\pi r^3\,.\,n\,.\,RT$. The probability that a sphere of radius $r$ surrounding A contains no other molecules is therefore $e^{-W/RT}$, that is $e^{-4/3\pi r^3 n}$. The differential of this quantity with respect to $r$ and with a minus sign prefixed is obviously that probability that the nearest neighbour of A lies at a distance between $r$ and $r+dr$ from it. Hence $P(r)\,dr=e^{-4/3\pi r^3 n}\,.\,4\pi r^2\,.\,n\,dr$.

Multiplying this by $r$ and integrating, we have

$$\lambda=\int_0^\infty e^{-4/3\pi n r^3}\,.\,4\pi r^3\,.\,n\,dr. \quad . \quad . \quad . \quad . \quad (2)$$

Writing $x=4/3\pi n r^3$, this may be evaluated thus

$$\lambda=\left(\frac{3}{4\pi n}\right)^{1/3}\int_0^\infty x^{1/3}e^{-x}\,dx=\left(\frac{3}{4\pi n}\right)^{1/3}\Gamma\left(\frac{4}{3}\right)=0{\cdot}554n^{-1/3}.$$

$$. \quad . \quad . \quad . \quad . \quad (3)$$

The same result is obtained by Hertz and by Gans in a different way (*loc. cit.*).

An *approximate* value of $\lambda$ may be obtained very simply as follows :—The probability that a molecule will be found at a distance between $r$ and $r+dr$ from molecule A is $4\pi r^2 n\,.\,dr$. For small values of $r$ we may, without serious error, take the probability of just one molecule being found within a sphere of radius $r$ drawn round A as centre to be simply $\int_0^r 4\pi r^2 n\,.\,dr$. The mean distance between A and its neighbour is the radius of the sphere for which this probability is unity. Thus $\lambda=r$, where $4/3\pi n r^3=1$. Hence $\lambda=\left(\frac{3}{4\pi n}\right)^{1/3}=0{\cdot}62n^{-1/3}$, which does not differ very greatly from the accurate value given above.

### 3. *The Case of Dense Fluids.*

The preceding discussion makes it clear that for the same density a chaotic distribution of the molecules gives a considerably smaller value for the mean distance between neighbours than a regular ordering in space. According to the thermodynamic theory of density fluctuations in fluids developed by Smoluchowski and Einstein, a highly compressible fluid, *e. g.*, a gas, exhibits greater relative fluctuations of density—that is, greater irregularities in the space-arrangement of the molecules—than a relatively incompressible one, *e. g.*, a liquid at ordinary temperatures and pressures, and the study of the scattering of light and of X-rays in fluids fully substantiates this. Hence, it is seen that, in the formula $\lambda = k \,.\, n^{-1/3}$, $k$ should have a larger value for the liquid than for the gaseous state; it may indeed be expected that the value of $k$ in liquids approaches pretty closely the value unity characteristic of a cubical ordering in space.

For dense fluids, as in gases, we have

$$\lambda = \int_0^\infty r\,\mathrm{P}(r)\,dr.$$

The problem is to find the form of the function $\mathrm{P}(r)$. If $\sigma$ be the diameter of a molecule, $\mathrm{P}(r)$ obviously vanishes when $r < \sigma$, hence we may write

$$\lambda = \int_\sigma^\infty r\,\mathrm{P}(r)\,dr. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let $\mathrm{W}(r)$ denote the work required to create a spherical cavity of radius $r$ with the molecule A at its centre. $\mathrm{W}(r)$ vanishes when $r = \sigma$. Applying Boltzmann's principle, we have, as before, $\mathrm{P}(r)\,dr = e^{-\mathrm{W}(r)/\mathrm{RT}} \,.\, \mathrm{W}'(r)/\mathrm{RT} \,.\, dr$, and

$$\lambda = \int_\sigma^\infty r \,.\, e^{-\frac{\mathrm{W}(r}{\mathrm{RT}}} \,.\, \mathrm{W}'(r) \,.\, \frac{1}{\mathrm{RT}} \,.\, dr. \quad . \quad . \quad . \quad (5)$$

If we denote the pressure per unit area on the wall of the cavity by $\mathrm{RT}\phi(r)$, then

$$\mathrm{W}'(r)\,dr = 4\pi r^2 \,.\, \mathrm{RT}\phi(r) \,.\, dr,$$

and

$$\lambda = \int_\sigma^\infty e^{-\int_\sigma^r 4\pi r^2 \phi(r)\,dr} \,.\, 4\pi r^3 \phi(r)\,dr. \quad . \quad . \quad . \quad (6)$$

The total pressure $4\pi r^2 \,.\, \phi(r) \,.\, \mathrm{RT}$ on the surface of the spherical cavity is obviously due to, ($a$) the impact of

the molecules outside the cavity on its boundary, and (*b*) the resultant of the attractions of the molecules outside the cavity on each other and on the molecule at its centre ; in a dense fluid, owing to the proximity of the molecules, these attractions may be very considerable, as is well known. To enable $\lambda$ to be evaluated, we may as a first approximation take $\phi(r)$ to be equal to a constant $\Phi$. We then write

$$\lambda=\int_{\sigma}^{\infty} e^{-4/3\pi(r^3-\sigma^3)\Phi}\,.\,4\pi r^3\,.\,\Phi\,.\,dr. \quad . \quad . \quad . \quad (7)$$

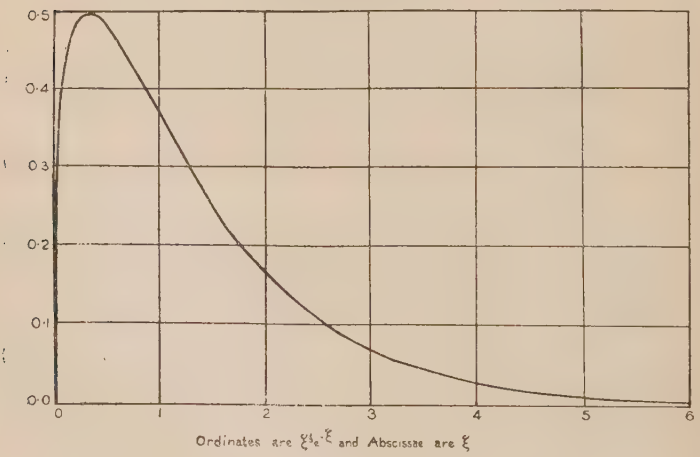
Putting $4/3\pi r^3\,.\,\Phi=\xi$ and $4/3\pi\sigma^3\,.\,\Phi=\eta$, we have

$$\lambda=e^{\eta}\int_{\eta}^{\infty} r\,.\,e^{-\xi}d\xi=\left(\frac{3}{4\pi\Phi}\right)^{1/3}\,.\,e^{\eta}\int_{\eta}^{\infty}\xi^{1/3}\,.\,e^{-\xi}\,d\xi \quad . \quad (8)$$

$$=\sigma\,.\,\frac{e^{\eta}}{\eta^{1/3}}\int_{\eta}^{\infty}\xi^{1/3}e^{-\xi}\,d\xi. \quad . \quad . \quad . \quad . \quad (9)$$

The simplest way of evaluating (8) and (9) is by graphical and mechanical integration. The figure gives a graph of

Fig. 1.




Graph of $\xi^{1/3}\,e^{-\xi}$ as a function of $\xi$.

the function under integration between $\xi=0$ and $\xi=6$, from which it is seen that, except for very small values of the argument, the trend of the curve is practically exponential. When $\eta=0$, the integral is simply $\Gamma(4/3)$.

For small values of $\eta$, the integral is best determined by

finding the integral $\int_0^\eta \xi^{1.3} e^{-\xi}\, d\xi$ from the graph by aid of a planimeter and subtracting it from $\Gamma(4/3)$. For large values of $\eta$, the integral may be found directly from a graph of the exponential part of the curve drawn on a suitable scale. The table gives the values of $\lambda$ thus determined for different values of $\eta$ :—

*Table of Mean Distances.*

| $\frac{4\pi}{3}\sigma^3 . \Phi$ | 0·0 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 2·0 | 3·0 | 4·0 | 5·0 | 5·92 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\lambda . \Phi^{1.3}$... | 0·554 | 0 618 | 0·663 | 0·698 | 0·735 | 0·763 | 0·880 | 0·970 | 1·07 | 1·12 | 1·17 |
| $\lambda/\sigma$ ..... | $\infty$ | 1·70 | 1·45 | 1·34 | 1·28 | 1·23 | 1·13 | 1·09 | 1·08 | 1·07 | 1·06 |

For an ideal gas, $\Phi = n$, and we have from the table $\lambda = 0{\cdot}554 \times n^{-1/3}$ as already found. It is also seen that for increasing values of $\Phi$, $\lambda$ diminishes at first rather rapidly and later quite slowly as to approach the same value as the molecular diameter $\sigma$. How closely the mean distance between neighbouring molecules tends to approach the molecular diameter depends on the value of $\eta$, *i.e.*, on $\Phi(r)\mathrm{RT}$, which is the pressure per unit area on the walls of a spherical cavity of radius $r$ surrounding a specified molecule. As already remarked, the pressure is determined by the molecular impacts and also by the molecular attractions, and, in view of the uncertainty regarding the actual laws of attraction between molecules in the immediate vicinity of each other, any estimate of the magnitude of $\Phi$ is necessarily provisional. In any case, we are probably not very wide of the mark in taking $\Phi$ to be generally of the same order of magnitude as $n$, the number of molecules per unit of volume. If this assumption be justifiable, $\eta$ is comparable with $4/3\pi\sigma^3 . n$, that is, with eight times the space occupied by the molecular spheres in unit volume ; the second horizontal row of figures would give approximately the value of $k$, where $\lambda = k . n^{-1/3}$. For a closely packed assemblage of spheres, we know independently that $n . \sigma^3 = \sqrt{2}$ and $4/3\pi\sigma^3 . n = \eta = 5{\cdot}92$, and that $\lambda n^{1/3} = 1{\cdot}123$, and also that $\lambda/\sigma = 1{\cdot}00$. These values agree with the corresponding figures given in the table to within a few per cent.

### 4. *An Alternative Method.*

The problem may also be dealt with by the aid of Boltzmann's Distribution Law. In an ideal gas, the probability that a molecule will be found within the space between two contiguous concentric spheres of radii $r$ and $r+dr$ respectively is $4\pi r^2 . n . dr$. In a *dense* fluid, the probability in question is the same, if the centre of the spheres be an arbitrarily chosen *geometrical* point. If, however, the centre be the instantaneous position of some specified *molecule*, its presence must influence the distribution of molecules in its immediate neighbourhood. Let $\psi(r)$ be the work necessary to bring two molecules from infinity to a distance $r$ apart. Then the probability of their being found at a distance $r$ apart is less than the probability of their being out of range of each other's action in the ratio $e^{-\psi(r)/\mathrm{RT}}$. Thus we are led to modify the expression $4\pi r^2 . n . dr$ and write it in the form $4\pi r^2 n \chi(r)\, dr$, where $\chi(r)$ as a first approximation may be taken to be $e^{-\psi(r)/\mathrm{RT}}$; from the nature of the case it is clear that when $r<\sigma$, $\chi(r)$ vanishes, and that for large values of $r$, $\chi(r)$ becomes unity.

Considering now a particular molecule, let $\mathrm{P}(r)\, dr$ be the probability that the distance between it and its nearest *neighbour* is between $r$ and $r+dr$. Then the probability that there are no molecules at a distance between 0 and $r$ from it is $1-\int_0^r \mathrm{P}(r)\, dr$. The probability that there is a molecule between $r$ and $r+dr$ distant from it is $4\pi r^2 . n . \chi(r)$, where $\chi(r)$ is a function of $r$ depending on the intermolecular forces and the density of the fluid as remarked above. We may take the probability that the nearest molecule lies between $r$ and $r+dr$ to be equal to the product of the probabilities that there are no molecules between 0 and $r$, and that there is one molecule between $r$ and $r+dr$. Therefore

$$\left[1-\int_0^r \mathrm{P}(r)\, dr\right] 4\pi n r^2 \chi(r)\, dr = \mathrm{P}(r)\, dr.$$

This is the equation from which we may determine $\mathrm{P}(r)$. Differentiating with respect to $r$, we have

$$\frac{d}{dr}\cdot\frac{\mathrm{P}(r)}{4\pi r^2 . n\chi(r)} = -\frac{\mathrm{P}(r)}{4\pi r^2 . n\chi(r)} . 4\pi n r^2 \chi(r).$$

Integrating again, we have

$$\mathrm{P}(r) = 4\pi r^2 . n\chi(r) \; . e^{-\int_0^r 4\pi n r^2 \chi(r)\, dr} \times \text{constant}.$$

The value of the constant of integration is evidently 1, as, when $r$ is small, $P(r)=4\pi nr^2\chi(r)$. It follows that

$$\lambda=\int_{\sigma}^{\infty} 4\pi nr^3\chi(r)\,.\,e^{-\int_{\sigma}^{r}4\pi nr^2\chi(r)\,dr}\,.\,dr.$$

It will be noticed that the expression is of the same general form as that obtained previously, and the numerical discussion proceeds on identical lines.

If we make the special assumption that the molecular centres are distributed more or less uniformly in available space, even in the immediate neighbourhood of the specified molecule under consideration, then $\chi(r)=1$ and

$$\lambda=\int_{\sigma}^{\infty} e^{-4/3\pi n(r^3-\sigma^3)}\,.\,4\pi n\,.\,r^3\,.\,dr. \quad . \quad . \quad (10)$$

We have already discussed the evaluation of this integral (see (7) above). As in the case of an ideal gas, values of $\lambda$ agreeing pretty closely with those given by the complete formula may be obtained in the following way. The available space for the centres of other molecules within a sphere of radius $r$ round the centre of a specified molecule is $4/3\pi(r^3-\sigma^3)$. The probability of a molecule being found within this space is $4/3\pi n\,.\,(r^3-\sigma^3)$. The particular value of $r$ for which this probability is unity gives the mean distance $\lambda$ between neighbouring molecules. Thus

$$4/3\pi n(\lambda^3-\sigma^3)=1 \quad \text{and} \quad \lambda=\left(\frac{3}{4\pi n}+\sigma^3\right)^{1/3}. \quad . \quad (11)$$

For small values of the density, this gives $\lambda=0{\cdot}62\,.\,n^{-1/3}$ and for great values of the density $\lambda=\sigma$. The following table shows how closely the values of $\lambda$ obtained from formulæ (10) and (11) agree with each other:—

*Comparison between* (10) and (11).

| $4/3\pi n\,.\,\sigma^3$. | | 0·0 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 2·0 | 3·0 | 4·0 | 5·0 | 5·92 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\lambda\times n^{1/3}$ | (10) | 0·554 | 0·618 | 0·663 | 0·698 | 0·735 | 0·763 | 0·880 | 0·970 | 1·07 | 1·12 | 1·17 |
| | (11) | 0·620 | 0·659 | 0·694 | 0·725 | 0·754 | 0·781 | 0·894 | 0·984 | 1·06 | 1·13 | 1·18 |
| $\lambda/\sigma$ | (10) | $\infty$ | 1·70 | 1·45 | 1·34 | 1·28 | 1·23 | 1·13 | 1·09 | 1·08 | 1·07 | 1·06 |
| | (11) | $\infty$ | 1·82 | 1·52 | 1·38 | 1·31 | 1·26 | 1·14 | 1·09 | 1·08 | 1·06 | 1·04 |

It will be noted that the rough formula gives practically the same values for $\lambda$ as the more elaborate calculation.

### 5. *Remarks on Gans's Paper.*

Finally, a few words will not be out of place regarding the treatment of the problem by R. Gans in the paper already cited. He takes the molecules to be spheres of diameter $\sigma$ and takes the probability that two molecules will be found at a specified distance $r$ apart to be given by the expression

$$4\pi r^2 . n dr \left[1 + \frac{b}{\mathrm{V}} + \frac{5}{8}\left(\frac{b}{\mathrm{V}}\right)^2 + 0{\cdot}287\left(\frac{b}{\mathrm{V}}\right)^3 + \ldots\right],$$

where

$$\frac{b}{\mathrm{V}} = \frac{2}{3}\pi n\sigma^3.$$

This expression, as is well known, was obtained by Boltzmann, Happel, and others on the assumption that $r$ is practically identical with $\sigma$, that is for two molecules in collision, and is inapplicable when $r > \sigma$. Gans also ignores the effect of the van der Waal's attractive or cohesive forces on the relative position of the molecules in space. That this is not justifiable is, *prima facie*, clear from Boltzmann's Distribution Law ; that the ordering of the molecules in the space occupied by a fluid is not determined merely by its density as contemplated by Gans is made sufficiently evident by the facts regarding the scattering of light in liquids and in vapours, and especially by the phenomenon of the opalescence which develops as the critical temperature is approached. The discussion given in the foregoing pages indicates that the theory of density-fluctuations in fluids and the problem of the mean distance between neighbouring molecules are closely related to each other.

### 6. *Summary and Conclusion.*

(*a*) The paper considers the problem of determining the mean distance in question by two distinct methods. In the first, Boltzmann's thermodynamic principle of Entropy-Probability is applied, and the chance that the nearest neighbour of a given molecule is situated at a specified distance from it is expressed in terms of the work done in creating a spherical cavity round the molecule in question. In the second method, Boltzmann's Distribution Law for the molecular positions in space is employed. Expressions

for the mean distance which are formally analogous are given by the two methods.

(*b*) The mean distance $\lambda$ between neighbouring molecules is given by the formula $k \cdot n^{-1/3}$, where $n$ is the number of molecules in unit volume and $k$ is a fraction which varies from 0·554 for an ideal gas up to 1·12 for the closest packing. The value of $k$ for actual liquids may range from about 0·8 to 1·0. For dense fluids, $\lambda$ is of the same order of quantities as the molecular diameter, but may be 10 per cent. to 20 per cent. greater.

(*c*) Tolerably accurate values of $\lambda$ may be obtained by a very simple mathematical treatment.

The author's thanks are due to Mr. N. C. Mazumdar for assistance in the numerical calculations.

Calcutta,
October 10, 1923.

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LXII. *Certain Types of Elastic Stress which are peculiarly related to each of the several Curvilinear Orthogonal Coordinate Systems.* *By* R. F. Gwyther, *M.A.**

IN a paper † dealing with the Stress Equations referred to general orthogonal coordinates, I have shown that the six elements of stress can be expressed in either of two forms (the $\theta$-form and the $\psi$-form) in terms of three general and arbitrary functions.

In this paper I propose to make use of the values of the stresses in the $\theta$-form to investigate the conditions under which, when the stresses are elastic, the components of the displacement can be expressed in terms of the same three functions as the stresses, and to continue the discussion in the simpler of the cases concerned.

1. The values of S, T, U given in the paper just referred to are :—

$$\begin{aligned} \mathrm{S} &= h_2 h_3 \frac{\partial^2 \theta_1}{\partial \eta \, \partial \zeta} + \left( h_3 \frac{\partial h_2}{\partial \zeta} - \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \zeta} \right) \frac{\partial \theta_1}{\partial \eta} \\ &\quad + \left( h_2 \frac{\partial h_3}{\partial \eta} - \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \eta} \right) \frac{\partial \theta_1}{\partial \zeta}, \\ \mathrm{T} &= \frac{h_1 h_3}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial \theta_1}{\partial \zeta}, \\ \mathrm{U} &= \frac{h_1 h_2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial \theta_1}{\partial \eta}, \end{aligned} \quad \ldots \ldots \ldots \quad (1)$$

as far as $\theta_1$ and its differential coefficients are concerned.

* Communicated by the Author.

† Phil. Mag. September 1923, p. 481.

The values are ultimately to be completed by a process of cyclical interchange, so as to include the terms in $\theta_2$ and $\theta_3$. Writing the components of the displacement as $u$, $v$, $w$, the necessary conditions include

$$\left.\begin{aligned} \mathrm{S} = na &= n\left\{\frac{h_2}{h_3}\frac{\partial(h_3 w)}{\partial\eta} + \frac{h_3}{h_2}\frac{\partial(h_2 v)}{\partial\zeta}\right\},\\ \mathrm{T} = nb &= n\left\{\frac{h_3}{h_1}\frac{\partial(h_1 u)}{\partial\zeta} + \frac{h_1}{h_3}\frac{\partial(h_3 w)}{\partial\xi}\right\},\\ \mathrm{U} = nc &= n\left\{\frac{h_1}{h_2}\frac{\partial(h_2 v)}{\partial\xi} + \frac{h_2}{h_1}\frac{\partial(h_1 u)}{\partial\eta}\right\}. \end{aligned}\right\} \quad . \quad . \quad (2)$$

There is only one case in which these conditions can be satisfied absolutely, which is when

$$\theta_1 = \theta_2 = \theta_3 = \phi,$$

and

$$2nu = h_1\frac{\partial\phi}{\partial\xi}, \quad 2nv = h_2\frac{\partial\phi}{\partial\eta}, \quad 2nw = h_3\frac{\partial\phi}{\partial\zeta}. \quad . \quad (3)$$

In the general case, which will be contingent, the mode in which the differential coefficients of the $\theta$'s enter the values of the components of the displacement are fairly obvious, and must reduce to those in (3), when the $\theta$'s are all made equal.

We therefore shall write in the most general case :

$$\left.\begin{aligned} 2nu &= h_1\frac{\partial}{\partial\xi}(\theta_2+\theta_3-\theta_1) + \alpha_3(\theta_3-\theta_1) - \alpha_2(\theta_1-\theta_2),\\ 2nv &= h_2\frac{\partial}{\partial\eta}(\theta_3+\theta_1-\theta_2) + \beta_1(\theta_1-\theta_2) - \beta_3(\theta_2-\theta_3),\\ 2nw &= h_3\frac{\partial}{\partial\zeta}(\theta_1+\theta_2-\theta_3) + \gamma_2(\theta_2-\theta_3) - \gamma_1(\theta_3-\theta_1), \end{aligned}\right\} \quad . \quad (4)$$

in which a cyclical symmetry is effected.

On substitution, the first of the conditions (2) becomes

$$\begin{aligned} 0 = &\left(\frac{\beta_1}{h_2}+\frac{2}{h_1}\frac{\partial h_1}{\partial\eta}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\zeta} - \left(\frac{\gamma_1}{h_3}+\frac{2}{h_1}\frac{\partial h_1}{\partial\zeta}\right)\frac{\partial(\theta_3-\theta_1)}{\partial\eta}\\ &+\left(\frac{\gamma_2}{h_3}-\frac{2}{h_2}\frac{\partial h_2}{\partial\zeta}\right)\frac{\partial(\theta_2-\theta_3)}{\partial\eta} - \left(\frac{\beta_3}{h_2}-\frac{2}{h_3}\frac{\partial h_3}{\partial\eta}\right)\frac{\partial(\theta_2-\theta_3)}{\partial\zeta}\\ &+\frac{1}{h_2^2}\frac{\partial(h_2\beta_1)}{\partial\zeta}(\theta_1-\theta_2) - \frac{1}{h_3^2}\frac{\partial(h_3\gamma_1)}{\partial\eta}(\theta_3-\theta_1)\\ &+\left\{\frac{1}{h_3^2}\frac{\partial(h_3\gamma_2)}{\partial\eta} - \frac{1}{h_2^2}\frac{\partial(h_2\beta_3)}{\partial\zeta}\right\}(\theta_2-\theta_3) \quad . \quad . \quad . \quad (5) \end{aligned}$$

The other two equations of condition may be written down by a process of cyclical interchange.

2. The three conditions for elastic equilibrium which I shall select for preliminary consideration are no doubt simpler than the remaining three, and my next step will be to simplify the form of the conditions expressed in (5) by the selection of values for the six arbitrary constants contained in them. The selection decided upon must find its support in the sequel.

The choice made is that the coefficients of $\partial(\theta_1-\theta_2)/\partial\zeta$, $\partial(\theta_3-\theta_1)/\partial\eta$, and of similar terms in the other equations shall be made null ; that is, I make

$$\beta_1=-\frac{2h_2}{h_1}\frac{\partial h_1}{\partial\eta}; \quad \gamma_2=-2\frac{h_3}{h_2}\frac{\partial h_2}{\partial\zeta}; \quad \alpha_3=-2\frac{h_1}{h_3}\frac{\partial h_2}{\partial\xi};$$

$$\gamma_1=-\frac{2h_3}{h_1}\frac{\partial h_1}{\partial\zeta}; \quad \alpha_2=-2\frac{h_1}{h_2}\frac{\partial h_2}{\partial\xi}; \quad \beta_3=-2\frac{h_2}{h_3}\frac{\partial h_3}{\partial\eta}. \quad . \quad (6)$$

The first of the conditions (5) thus becomes

$$2\left(\frac{1}{h_3}\frac{\partial h_3}{\partial\eta}\frac{\partial}{\partial\zeta}-\frac{1}{h_2}\frac{\partial h_2}{\partial\zeta}\frac{\partial}{\partial\eta}\right)(\theta_2-\theta_3)$$

$$-\frac{1}{h_2^2}\frac{\partial}{\partial\zeta}\left(\frac{h_2^2}{h_1}\frac{\partial h_1}{\partial\eta}\right)(\theta_1-\theta_2)+\frac{1}{h_3^2}\frac{\partial}{\partial\eta}\left(\frac{h_3^2}{h_1}\frac{\partial h_1}{\partial\zeta}\right)(\theta_3-\theta_1)$$

$$+\left\{\frac{1}{h_2^2}\frac{\partial}{\partial\zeta}\left(\frac{h_2^2}{h_3}\frac{\partial h_3}{\partial\eta}\right)-\frac{1}{h_3^2}\frac{\partial}{\partial\eta}\left(\frac{h_3^2}{h_2}\frac{\partial h_2}{\partial\zeta}\right)\right\}(\theta_2-\theta_3)=0. \quad (7)$$

By the use of Lamé's Identities, quoted in the paper previously referred to, this may be written

$$2\left(h_2\frac{\partial h_3}{\partial\eta}\frac{\partial}{\partial\zeta}-h_3\frac{\partial h_2}{\partial\zeta}\frac{\partial}{\partial\eta}\right)(\theta_2-\theta_3)-\frac{h_2h_3}{h_1^2}\frac{\partial h_1}{\partial\eta}\frac{\partial h_1}{\partial\zeta}(2\theta_1-\theta_2-\theta_3)$$

$$+\left\{h_2\frac{\partial^2h_3}{\partial\eta\,\partial\zeta}-h_3\frac{\partial^2h_2}{\partial\eta\,\partial\zeta}+\frac{h_3}{h_2}\frac{\partial h_2}{\partial\eta}\frac{\partial h_2}{\partial\zeta}-\frac{h_2}{h_3}\frac{\partial h_3}{\partial\eta}\frac{\partial h_3}{\partial\zeta}\right.$$

$$\left.+\frac{h_3}{h_1}\frac{\partial h_1}{\partial\eta}\frac{\partial h_2}{\partial\zeta}-\frac{h_2}{h_1}\frac{\partial h_1}{\partial\zeta}\frac{\partial h_3}{\partial\eta}\right\}(\theta_2-\theta_3)=0, \quad . \quad . \quad . \quad (8)$$

with two homologous equations.

These give relations between the differences of the three functions on which the stress-system depends and the particular orthogonal coordinate system to which the stress-system is referred.

The components of the displacement, as far as terms in $\theta_1$ are concerned, are from (4)

$$2nu = -h_1\frac{\partial\theta_1}{\partial\xi} + 2\left\{\frac{h_1}{h_2}\frac{\partial h_2}{\partial\xi} + \frac{h_1}{h_3}\frac{\partial h_3}{\partial\xi}\right\}\theta_1,$$

$$2nv = h_2\frac{\partial\theta_1}{\partial\eta} - 2\frac{h_2}{h_1}\frac{\partial h_1}{\partial\eta}\theta_1,$$

$$2nw = h_3\frac{\partial\theta_1}{\partial\zeta} - 2\frac{h_3}{h_1}\frac{\partial h_1}{\partial\zeta}\theta_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and it is in this form that they will be used later.

The general statement of these components I shall make in the form

$$2nu = h_1h_2h_3\frac{\partial}{\partial\xi}\frac{\theta_2+\theta_3-\theta_1}{h_2h_3} + \frac{h_1}{h_2}\frac{\partial h_2}{\partial\xi}(\theta_3+\theta_1-\theta_2) + \frac{h_1}{h_3}\frac{\partial h_3}{\partial\xi}(\theta_1+\theta_2-\theta_3),$$

with two homologous expressions for $2nv$ and $2nw$.

. . . (10)

3. There remain three other conditions necessary for elastic equilibrium, which may conveniently be stated in the form

$$P-Q = 2n(e-f), \qquad R-P = 2n(g-e),$$

with

$$P+Q+R = (3m-n)(e+f+g).$$

The values of P and Q obtained in my previous paper, as far as the function $\theta_1$ is concerned, are :

$$P = 2\frac{h_1^2}{h_2h_3}\frac{\partial h_2}{\partial\xi}\frac{\partial h_3}{\partial\xi}\theta_1,$$

$$Q = -h_3^2\frac{\partial^2\theta_1}{\partial\zeta^2} - \frac{h_1^2}{h_3}\frac{\partial h_3}{\partial\xi}\frac{\partial\theta_1}{\partial\xi} + \frac{h_2^2}{h_3}\frac{\partial h_3}{\partial\eta}\frac{\partial\theta_1}{\partial\eta} + \left(2\frac{h_3^2}{h_1}\frac{\partial h_1}{\partial\zeta} - h_3\frac{\partial h_3}{\partial\zeta}\right)\frac{\partial\theta_1}{\partial\zeta}$$

$$+ 2\left\{\frac{h_3^2}{h_1}\frac{\partial^2 h_1}{\partial\zeta^2} - \left(2\frac{h_3^2}{h_1^2}\frac{\partial h_1}{\partial\zeta} - \frac{h_3}{h_1}\frac{\partial h_3}{\partial\zeta}\right)\frac{\partial h_1}{\partial\zeta} - \frac{h_2^2}{h_1h_3}\frac{\partial h_1}{\partial\eta}\frac{\partial h_3}{\partial\eta}\right\}\theta_1.$$

. . . (11)

The value of R can be obtained from that of Q by exchanging $h_2$ and $h_3$, $\eta$ and $\zeta$, while retaining $h_1$ and $\xi$.

All the values can then be completed by a general cyclical interchange.

The value of $e$ is given

$$e = h_1\frac{\partial u}{\partial \xi} - \frac{h_2}{h_1}\frac{\partial h_1}{\partial \eta}v - \frac{h_3}{h_1}\frac{\partial h_1}{\partial \zeta}w,$$

and there are homologous expressions for $f$ and $g$, in which we are to substitute for $u$, $v$, $w$ from (9).

Thus we find

$$\begin{aligned}
2ne = &-h_1^2\frac{\partial^2\theta_1}{\partial\xi^2} - \left(h_1\frac{\partial h_1}{\partial\xi} - 2\frac{h_1^2}{h_2}\frac{\partial h_2}{\partial\xi} - 2\frac{h_1^2}{h_3}\frac{\partial h_3}{\partial\xi}\right)\frac{\partial\theta_1}{\partial\xi} \\
&\qquad - \frac{h_2^2}{h_1}\frac{\partial h_1}{\partial\eta}\frac{\partial\theta_1}{\partial\eta} - \frac{h_3^2}{h_1}\frac{\partial h_1}{\partial\zeta}\frac{\partial\theta_1}{\partial\zeta} \\
&+ 2\theta_1\left\{\frac{h_1^2}{h_2}\frac{\partial^2 h_2}{\partial\xi^2} + \frac{h_1^2}{h_3}\frac{\partial^2 h_3}{\partial\xi^2} + \left(\frac{h_1}{h_2}\frac{\partial h_1}{\partial\xi} - \frac{h_1^2}{h_2^2}\frac{\partial h_2}{\partial\xi}\right)\frac{\partial h_2}{\partial\xi}\right. \\
&+ \left(\frac{h_1}{h_3}\frac{\partial h_1}{\partial\xi} - \frac{h_1^2}{h_3^2}\frac{\partial h_3}{\partial\xi}\right)\frac{\partial h_3}{\partial\xi} + \frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial\eta}\right)^2 + \frac{h_3^2}{h_1^2}\left(\frac{\partial h_1}{\partial\zeta}\right)^2\Big\}, \\
2nf = &\ h_2^2\frac{\partial^2\theta_1}{\partial\eta^2} + \frac{h_1^2}{h_2}\frac{\partial h_2}{\partial\xi}\frac{\partial\theta_1}{\partial\xi} + \left(h_2\frac{\partial h_2}{\partial\eta} - 2\frac{h_2^2}{h_1}\frac{\partial h_1}{\partial\eta}\right)\frac{\partial\theta_1}{\partial\eta} - \frac{h_3^2}{h_2}\frac{\partial h_2}{\partial\zeta}\frac{\partial\theta_1}{\partial\zeta} \\
&- 2\theta_1\left\{\frac{h_2^2}{h_1}\frac{\partial^2 h_1}{\partial\eta^2} + \left(\frac{h_2}{h_1}\frac{\partial h_2}{\partial\eta} - \frac{h_2^2}{h_1^2}\frac{\partial h_1}{\partial\eta}\right)\frac{\partial h_1}{\partial\eta}\right. \\
&+ \left(\frac{h_1^2}{h_2^2}\frac{\partial h_2}{\partial\xi} + \frac{h_1^2}{h_2 h_3}\frac{\partial h_3}{\partial\xi}\right)\frac{\partial h_2}{\partial\xi} - \frac{h_3^2}{h_1 h_2}\frac{\partial h_1}{\partial\zeta}\frac{\partial h_2}{\partial\zeta}\Big\}, \\
2ng = &\ h_3^2\frac{\partial^2\theta_1}{\partial\zeta^2} + \frac{h_1^2}{h_3}\frac{\partial h_3}{\partial\xi}\frac{\partial\theta_1}{\partial\xi} - \frac{h_2^2}{h_3}\frac{\partial h_3}{\partial\eta}\frac{\partial\theta_1}{\partial\eta} + \left(h_3\frac{\partial h_3}{\partial\zeta} - \frac{2h_3^2}{h_1}\frac{\partial h_1}{\partial\zeta}\right)\frac{\partial\theta_1}{\partial\zeta} \\
&- 2\theta_1\left\{\frac{h_3^2}{h_1}\frac{\partial^2 h_1}{\partial\xi^2} + \left(\frac{h_3}{h_1}\frac{\partial h_3}{\partial\zeta} - \frac{h_3^2}{h_1^2}\frac{\partial h_1}{\partial\zeta}\right)\frac{\partial h_1}{\partial\zeta}\right. \\
&+ \left(\frac{h_1^2}{h_3^2}\frac{\partial h_3}{\partial\xi} + \frac{h_1^2}{h_2 h_3}\frac{\partial h_2}{\partial\xi}\right)\frac{\partial h_3}{\partial\xi} - \frac{h_2^2}{h_1 h_3}\frac{\partial h_1}{\partial\eta}\frac{\partial h_3}{\partial\eta}\Big\} \quad . \quad . \quad (12)
\end{aligned}$$

as far as $\theta_1$ is concerned.

Combining these values with those given for P, Q, R in (10), and using Lamé's Identities, the simplifications are notable, and we find

$$\begin{aligned}
\mathrm{P}-\mathrm{Q}-2n(e-f) = &\ \nabla^2\theta_1 - 2\theta_1\left\{2\frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial\eta}\right)^2 + 2\frac{h_1^2}{h_3^2}\left(\frac{\partial h_2}{\partial\xi}\right)^2\right. \\
&\left. + \frac{h_3^2}{h_1^2}\left(\frac{\partial h_1}{\partial\zeta}\right)^2 + \frac{h_1^2}{h_3^2}\left(\frac{\partial h_3}{\partial\xi}\right)^2\right\}, \\
\mathrm{R}-\mathrm{P}-2n(g-e) = &-\nabla^2\theta_1 + 2\theta_1\left\{\frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial\eta}\right)^2 + \frac{h_1^2}{h_2^2}\left(\frac{\partial h_2}{\partial\xi}\right)^2\right. \\
&\left. + 2\frac{h_3^2}{h_1^2}\left(\frac{\partial h_1}{\partial\zeta}\right)^2 + 2\frac{h_1^2}{h_3^2}\left(\frac{\partial h_3}{\partial\xi}\right)^2\right\},
\end{aligned}$$

whence

$$Q-R-2n(f-g)=2\theta_1\left\{\frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial \eta}\right)^2+\frac{h_1^2}{h_2^2}\left(\frac{\partial h_2}{\partial \xi}\right)^2 -\frac{h_3^2}{h_1^2}\left(\frac{\partial h_1}{\partial \zeta}\right)-\frac{h_1^2}{h_3^2}\left(\frac{\partial h_3}{\partial \xi}\right)^2\right\}\ldots \quad (13)$$

By completing $P-Q-2n(e-f)$ so as to include terms in $\theta_2$ and $\theta_3$, we find

$$\nabla^2(\theta_1-\theta_2)-4(\theta_1-\theta_2)\left\{\frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial \eta}\right)^2+\frac{h_1^2}{h_2^2}\left(\frac{\partial h_2}{\partial \xi}\right)^2\right\} +2(\theta_2-\theta_3)\left\{\frac{h_3^2}{h_2^2}\left(\frac{\partial h_2}{\partial \zeta}\right)^2+\frac{h_2^2}{h_3^2}\left(\frac{\partial h_3}{\partial \eta}\right)^2\right\} +2(\theta_3-\theta_1)\left\{\frac{h_3^2}{h_2^2}\left(\frac{\partial h_1}{\partial \zeta}\right)^2+\frac{h_1^2}{h_3^2}\left(\frac{\partial h_3}{\partial \xi}\right)^2\right\}=0$$

with homologous equations. . (14)

4. The last condition to be satisfied is

$$P+Q+R=(3m-n)(e+f+g).$$

We find from (11) that

$$\begin{aligned}&P+Q+R\\ &=-\nabla^2(\theta_1+\theta_2+\theta_3)+h_1h_2h_3\left\{\frac{\partial}{\partial \xi}\left(\frac{h_1}{h_2h_3}\frac{\partial \theta_1}{\partial \xi}\right)+\frac{\partial}{\partial \eta}\left(\frac{h_2}{h_3h_1}\frac{\partial \theta_2}{\partial \eta}\right)\right.\\ &\qquad\left.+\frac{\partial}{\partial \zeta}\left(\frac{h_3}{h_1h_2}\frac{\partial \theta_3}{\partial \zeta}\right)\right\}\\ &-\left(\frac{h_1^2}{h_2}\frac{\partial h_2}{\partial \xi}\frac{\partial}{\partial \xi}-\frac{h_2^2}{h_1}\frac{\partial h_1}{\partial \eta}\frac{\partial}{\partial \eta}\right)(\theta_1-\theta_2)\\ &-\left(\frac{h_2^2}{h_3}\frac{\partial h_3}{\partial \eta}\frac{\partial}{\partial \eta}-\frac{h_3^2}{h_2}\frac{\partial h_2}{\partial \zeta}\frac{\partial}{\partial \zeta}\right)(\theta_2-\theta_3)\\ &-\left(\frac{h_3^2}{h_1}\frac{\partial h_1}{\partial \zeta}\frac{\partial}{\partial \zeta}-\frac{h_1^2}{h^3}\frac{\partial h_3}{\partial \xi}\frac{\partial}{\partial \xi}\right)(\theta_3-\theta_1)\\ &+2A_1\theta_1+2A_2\theta_2+2A_3\theta_3 \quad \ldots \quad (15)\end{aligned}$$

where

$$\begin{aligned}A_1=&\frac{h_2^2}{h_1}\frac{\partial^2 h_1}{\partial \eta^2}-2\frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial \eta}\right)^2+\frac{h_2}{h_1}\frac{\partial h_1}{\partial \eta}\frac{\partial h_2}{\partial \eta}-\frac{h_2^2}{h_1h_3}\frac{\partial h_1}{\partial \eta}\frac{\partial h_3}{\partial \eta}\\ &+\frac{h_3^2}{h_1}\frac{\partial^2 h_1}{\partial \zeta^2}-2\frac{h_3^2}{h_1^2}\left(\frac{\partial h_1}{\partial \zeta}\right)^2-\frac{h_3^2}{h_1h_2}\frac{\partial h_1}{\partial \zeta}\frac{\partial h_2}{\partial \zeta}+\frac{h_3}{h_1}\frac{\partial h_1}{\partial \zeta}\frac{\partial h_3}{\partial \zeta}\\ &+\frac{h_1^2}{h_2h_3}\frac{\partial h_2}{\partial \xi}\frac{\partial h_3}{\partial \xi},\end{aligned}$$

or

$$= -\left\{\frac{h_1^2}{h_2}\frac{\partial^2 h_2}{\partial \xi^2} + \frac{h_1}{h_2}\frac{\partial h_1}{\partial \xi}\frac{\partial h_2}{\partial \xi} - 2\frac{h_1^2}{h_2^2}\left(\frac{\partial h_2}{\partial \xi}\right)^2 + \frac{h_1^2}{h_3}\frac{\partial^2 h_3}{\partial \xi^2} + \frac{h_1}{h_3}\frac{\partial h_1}{\partial \xi}\frac{\partial h_3}{\partial \xi} - 2\frac{h_1^2}{h_3^2}\left(\frac{\partial h_3}{\partial \xi}\right)^2 - \frac{h_1^2}{h_2 h_3}\frac{\partial h_2}{\partial \xi}\frac{\partial h_3}{\partial \xi}\right\},$$

by Lamé's Identities.

By adding these two values is found the value of $2A_1$ in the form presenting itself in the next paragraph.

The expressions for $A_2$ and $A_3$ are homologous to that for $A_1$.

Similarly, we find from (12):

$$\begin{aligned}
&2n(e+f+g)\\
&= \nabla^2(\theta_1+\theta_2+\theta_3) - 2h_1h_2h_3\left\{\frac{\partial}{\partial \xi}\left(\frac{h_1}{h_2h_3}\frac{\partial \theta_1}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h_2}{h_3h_1}\frac{\partial \theta_2}{\partial \eta}\right) + \frac{\partial}{\partial \zeta}\left(\frac{h_3}{h_1h_2}\frac{\partial \theta_3}{\partial \zeta}\right)\right\}\\
&\quad + 2\left(\frac{h_1^2}{h_2}\frac{\partial h_2}{\partial \xi}\frac{\partial}{\partial \xi} - \frac{h_2^2}{h_1}\frac{\partial h_1}{\partial \eta}\frac{\partial}{\partial \eta}\right)(\theta_1-\theta_2)\\
&\quad + 2\left(\frac{h_2^2}{h_3}\frac{\partial h_3}{\partial \eta}\frac{\partial}{\partial \eta} - \frac{h_3^2}{h_2}\frac{\partial h_2}{\partial \zeta}\frac{\partial}{\partial \zeta}\right)(\theta_2-\theta_3)\\
&\quad + 2\left(\frac{h_3^2}{h_1}\frac{\partial h_1}{\partial \zeta}\frac{\partial}{\partial \zeta} - \frac{h_1^2}{h_3}\frac{\partial h_3}{\partial \xi}\frac{\partial}{\partial \xi}\right)(\theta_3-\theta_1)\\
&\quad - 4A_1\theta_1 - 4A_2\theta_2 - 4A_3\theta_3. \qquad \ldots\ldots\ldots \quad (16).
\end{aligned}$$

The condition which we seek therefore becomes

$$\begin{aligned}
&(3m+n)\nabla^2(\theta_1+\theta_2+\theta_3)\\
&= 6m\left[h_1h_2h_3\left\{\frac{\partial}{\partial \xi}\left(\frac{h_1}{h_2h_3}\frac{\partial \theta_1}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\frac{h_2}{h_3h_1}\frac{\partial \theta_2}{\partial \eta}\right) + \frac{\partial}{\partial \zeta}\left(\frac{h_3}{h_1h_2}\frac{\partial \theta_3}{\partial \zeta}\right)\right\}\right.\\
&\quad - \left(\frac{h_1^2}{h_2}\frac{\partial h_2}{\partial \xi}\frac{\partial}{\partial \xi} - \frac{h_2^2}{h_1}\frac{\partial h_1}{\partial \eta}\frac{\partial}{\partial \eta}\right)(\theta_1-\theta_2)\\
&\quad - \left(\frac{h_2^2}{h_3}\frac{\partial h_3}{\partial \eta}\frac{\partial}{\partial \eta} - \frac{h_3^2}{h_2}\frac{\partial h_2}{\partial \zeta}\frac{\partial}{\partial \zeta}\right)(\theta_2-\theta_3)\\
&\quad - \left(\frac{h_3^2}{h_1}\frac{\partial h_1}{\partial \zeta}\frac{\partial}{\partial \zeta} - \frac{h_1^2}{h_3}\frac{\partial h_3}{\partial \xi}\frac{\partial}{\partial \xi}\right)(\theta_3-\theta_1)\\
&\quad \left. + 2A_1\theta_1 + 2A_2\theta_2 + 2A_3\theta_3\right] \qquad \ldots\ldots\ldots \quad (17).
\end{aligned}$$

If we write

$$2A_1 = 2\frac{h_1^2}{h_2h_3}\frac{\partial h_2}{\partial \xi}\frac{\partial h_3}{\partial \xi} + B_3 - B_2,$$

where

$$B_3 = \frac{h_2^2}{h_1^2}\frac{\partial^2 h_1}{\partial \eta^2} - \frac{h_1^2}{h_2}\frac{\partial h_2}{\partial \xi^2} - 2\frac{h_2^2}{h_1^2}\left(\frac{\partial h_1}{\partial \eta}\right)^2 + 2\frac{h_1^2}{h_2^2}\left(\frac{\partial h_2}{\partial \xi}\right)^2$$
$$+ \frac{h_2}{h_1}\frac{\partial h_1}{\partial \eta}\frac{\partial h_2}{\partial \eta} - \frac{h_1}{h_2}\frac{\partial h_1}{\partial \xi}\frac{\partial h_2}{\partial \xi} - \frac{h_3^2}{h_1h_2}\frac{\partial h_1}{\partial \zeta}\frac{\partial h_2}{\partial \zeta},$$

$$B_2 = \frac{h_1^2}{h_3}\frac{\partial^2 h_3}{\partial \xi^2} - \frac{h_3}{h_1}\frac{\partial h_1}{\partial \zeta^2} - 2\frac{h_1^2}{h_3^2}\left(\frac{\partial h_3}{\partial \xi}\right)^2 + 2\frac{h_3^2}{h_1}\left(\frac{\partial h_1}{\partial \zeta}\right)^2$$
$$+ \frac{h_1}{h_3}\frac{\partial h_1}{\partial \xi}\frac{\partial h_3}{\partial \xi} - \frac{h_3}{h_1}\frac{\partial h_1}{\partial \zeta}\frac{\partial h_3}{\partial \zeta} - \frac{h_2^2}{h_1h_3}\frac{\partial h_1}{\partial \eta}\frac{\partial h_3}{\partial \eta},$$

with similar expressions for $2A_2$ and $2A_3$,

we shall find

$$2A_1\theta_1 + 2A_2\theta_2 + 2A_3\theta_3$$
$$= 2\frac{h_1^2}{h_2h_3}\frac{\partial h_2}{\partial \xi}\frac{\partial h_3}{\partial \xi}\theta_1 + 2\frac{h_2^2}{h_1h_3}\frac{\partial h_1}{\partial \eta}\frac{\partial h_3}{\partial \eta}\theta_2 + 2\frac{h_3^2}{h_1h_2}\frac{\partial h_1}{\partial \zeta}\frac{\partial h_2}{\partial \zeta}\theta_3$$
$$+ B_1(\theta_2 - \theta_3) + B_2(\theta_3 - \theta_1) + B_3(\theta_1 - \theta_2),$$

for substitution in (17) if desired.

5. For a complete exposition, it would be necessary to employ the expressions for $u$, $v$, $w$ given in (4) to find $e, f, g$, and repeat the procedure in sections 3 and 4,—the constants taking finally values selected from

$$\beta_1 = \pm\frac{2h_2}{h_1}\frac{\partial h_1}{\partial \eta}, \quad \gamma_2 = \pm 2\frac{h_3}{h_2}\frac{\partial h_2}{\partial \zeta}, \quad \alpha_3 = \pm 2\frac{h_1}{h_2}\frac{\partial h_3}{\partial \xi},$$
$$\gamma_1 = \pm\frac{2h_3}{h_1}\frac{\partial h_1}{\partial \zeta}, \quad \alpha_2 = \pm 2\frac{h_1}{h_2}\frac{\partial h_2}{\partial \xi}, \quad \beta_2 = \pm 2\frac{h_2}{h_3}\frac{\partial h_3}{\partial \eta}.$$

As the results would meet contingencies, they would be valuable, but the process would be lengthy, and I have confined myself to one instance only, in which, however, the general method is fully exemplified.

The interest in general problems in orthogonal coordinate systems turns ultimately upon their application to the simpler of such systems, and I conclude by considering a few cases by the method of this paper. In all such cases I shall retain the coordinates $\xi$, $\eta$, $\zeta$ in the sense of the coordinates of the system.

I. *The cylindrical polar system.*

In this case we have

$$h_1 = 1, \quad h_2 = \frac{1}{\xi}, \quad h_3 = 1,$$

so that $\alpha_2$ is the only remaining constant.

The equations (5) reduce to

$$\left(\alpha_2 - \frac{2}{\xi}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\zeta} = 0, \quad \left(\alpha_2 + \frac{2}{\xi}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\eta} = 0.$$

The case which I have considered and to which equations (14) and (17) apply is when $\alpha_2 = 2/\xi$ and the condition becomes

$$\frac{\partial(\theta_1-\theta_2)}{\partial\eta} = 0.$$

There is another case which I have not considered when $\alpha_2 = -2/\xi$ and the condition becomes

$$\frac{\partial(\theta_1-\theta_2)}{\partial\zeta} = 0.$$

II. *The conjugate cylindric system.*

In this case

$$h_1 = h_2 = h = f(\xi, \eta), \quad h_3 = 1,$$

and $\beta_1$ and $\alpha_2$ are the only remaining constants.

The equations (5) now reduce to

$$\left(\beta_1 + 2\frac{\partial h}{\partial\eta}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\zeta} = 0,$$

$$\left(\alpha_2 + 2\frac{\partial h}{\partial\xi}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\zeta} = 0,$$

$$\left(\beta_1 - 2\frac{\partial h}{\partial\eta}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\xi} - \left(\alpha_2 - 2\frac{\partial h}{\partial\xi}\right)\frac{\partial(\theta_1-\theta_2)}{\partial\eta} = 0.$$

The case which has been considered is when $\beta_1 = -2\dfrac{\partial h}{\partial\eta}$, $\alpha_2 = -2\dfrac{\partial h}{\partial\xi}$, and then the condition is

$$\frac{\partial(\theta_1-\theta_2)}{\partial\xi}\frac{\partial h}{\partial\eta} - \frac{\partial(\theta_1-\theta_2)}{\partial\eta}\frac{\partial h}{\partial\xi} = 0,$$

or

$$\theta_1 - \theta_2 = f(h, \zeta).$$

Alternatively, if either $\beta_1 = 2\dfrac{\partial h}{\partial \eta}$ or $\alpha_2 = 2\dfrac{\partial h}{\partial \xi}$, we have

$$\frac{\partial(\theta_1-\theta_2)}{\partial \zeta} = 0, \quad \theta_1-\theta_2 = f(\xi, \eta).$$

If both $\beta_1 = 2\dfrac{\partial h}{\partial \eta}$ and $\alpha_2 = 2\dfrac{\partial h}{\partial \xi}$, this is the sole condition; otherwise $\theta_1-\theta_2$ is a function either of $\xi$ or of $\eta$.

III. *The spherical polar system.*

Here we have

$$h_1 = 1, \quad h_2 = \frac{1}{\xi}, \quad h_3 = \frac{1}{\xi \sin \eta},$$

and $\alpha_2$, $\alpha_3$, and $\beta_3$ are the remaining constants.

The equations (5) become

$$\left(\frac{\beta_3}{h_2} - \frac{2}{h_3}\frac{\partial h_3}{\partial \eta}\right)\frac{\partial(\theta_2-\theta_3)}{\partial \zeta} = 0,$$

$$\left(\frac{\alpha_2}{h_1} + \frac{2}{h_2}\frac{\partial h_2}{\partial \xi}\right)\frac{\partial(\theta_1-\theta_2)}{\partial \zeta} - \left(\frac{\alpha_3}{h_1} - \frac{2}{h_3}\frac{\partial h_3}{\partial \xi}\right)\frac{\partial(\theta_3-\theta_1)}{\partial \zeta} = 0,$$

$$\left(\frac{\alpha_3}{h_1} + \frac{2}{h_3}\frac{\partial h_3}{\partial \xi}\right)\frac{\partial(\theta_3-\theta_1)}{\partial \eta} - \left(\frac{\beta_3}{h_2} + \frac{2}{h_3}\frac{\partial h_3}{\partial \eta}\right)\frac{\partial(\theta_2-\theta_3)}{\partial \xi}$$
$$- \left(\frac{\alpha_2}{h_1} - \frac{2}{h_2}\frac{\partial h_2}{\partial \xi}\right)\frac{\partial(\theta_1-\theta_2)}{\partial \eta} + \frac{1}{h_1^2}\frac{\partial(h_1\alpha_3)}{\partial \eta}(\theta_3-\theta_1)$$
$$- \frac{1}{h_2^2}\frac{\partial(h_2\beta_3)}{\partial \xi}(\theta_2-\theta_3) - \frac{1}{h_1^2}\frac{\partial(h_1\alpha_2)}{\partial \eta}(\theta_1-\theta_2) = 0.$$

The values we are to take for $\alpha_2$, $\alpha_3$, $\beta_3$ are:

$$\alpha_2 = \mp 2\frac{h_1}{h_2}\frac{\partial h_2}{\partial \xi} = \pm\frac{2}{\xi},$$

$$\alpha_3 = \mp 2\frac{h_1}{h_3}\frac{\partial h_3}{\partial \xi} = \pm\frac{2}{\xi},$$

$$\beta_3 = \mp 2\frac{h_2}{h_3}\frac{\partial h_3}{\partial \eta} = \pm\frac{2\cot\eta}{\xi},$$

whence

$$\partial(h_1\alpha_3)/\partial\eta = 0, \quad \partial(h_1\alpha_2)/\partial\eta = 0.$$

In the case we have considered, the upper signs are to be

taken and the conditions become

$$\frac{\partial(\theta_2-\theta_3)}{\partial\zeta}=0, \qquad \frac{\partial(\theta_3-\theta_1)}{\partial\zeta}=0,$$
$$\frac{\partial(\theta_1-\theta_2)}{\partial\eta}-\cot\eta(\theta_2-\theta_3)=0.$$

None of the other cases have been considered.

We may describe the conditions (5) as expressing the antecedent condition that the characteristics of the stress system and of the coordinate system are not such as exclude the possibility of the elastic displacement being expressed in terms of the same three functions as the stress, the final conditions being expressed in (14) and (17).

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LXIII. *The Emission from an Incandescent Platinum Wire in Air.* *By* Prof. A. M. Tyndall, *D.Sc.*, *and* G. C. Grindley, *B.Sc.* (*Bristol*) *.

IT is well known that the mobility of the normal ions produced by the usual ionizing agencies in fairly dry dust-free air at atmospheric pressure is of the order of 1·8 cm./sec./volt/cm. for negative and 1·4 for positive ions. An apparent exception to this was found by McClelland † in the case of ions from an incandescent wire, an arc, or a flame. In his experiments an air current carried the ions into a metal tube, in which their mobility was determined by a method which Rutherford had used in the case of ions produced by uranium.

In the case of an incandescent wire, with which the present paper is concerned, McClelland found that the ionic mobility was small compared with that produced by X-rays, and that the hotter the wire the smaller was the mobility. Further the mobility, which was of the order of 0·01 to ·003 cm./sec., decreased with increase of distance from the source. McClelland concluded that each ion picked up molecules and formed a cluster which grew in size with age. Again, Rutherford ‡ made observations on the current between two plates, one of which was red hot; he concluded that the mobility of the positive ions from platinum may

* Communicated by the Authors.

† McClelland, Proc. Camb. Phil. Soc. x. p. 241 (1899).

‡ Rutherford, Phys. Rev. xiii. p. 321 (1901).

vary within wide limits, its average value decreasing with increasing distance between the plates.

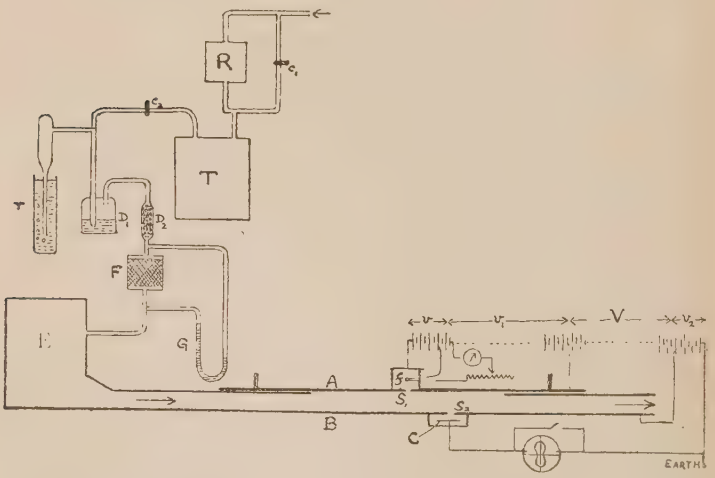
On general grounds it seemed probable that McClelland was dealing with a mixture of different types of ion, the relative proportions of which changed with time. For instance, several writers have referred to the particles of sputtered metal as nuclei to which some ions would attach themselves. The purpose of the following experiments was to obtain more definite information on the whole subject by means of mobility measurements.

Two types of apparatus were used: the first was suggested by an experiment of Nolan * (though differing from it in several respects), and is referred to below as the Box Method; the second was McClelland's original method with modifications.

*Box Method.*

A sketch of the apparatus is given in fig. 1.

Fig. 1.




A and B, the former in two parts, are brass sheets forming the top and bottom of a rectangular box 72 in. long and 10 in. wide. Except for the insertion of a glass window for observational purposes, the sides of the box were of ebonite about 2 in. deep. "$f$" is an incandescent platinum filament set up in a small side chamber placed on A over a slit $S_1$.

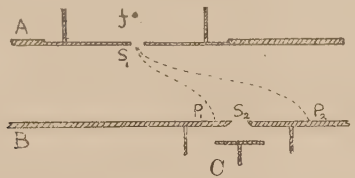
A stream of dry dust-free air is sent through the box. By electric fields of the appropriate sign and strength, ions

* Nolan, Proc. Roy. Irish Acad. xxxv. p. 38 (1920).

of either sign may be dragged from the vicinity of the wire down to $S_1$; those which drift into the air-stream may then be carried across it to the plate B.

Now, if more than one group of ions is present, the paths of these groups will be different. For example, if the ions consist of two groups, one of normal mobility and one of lower mobility, the first will travel along the dotted line striking B at the point $P_1$; the second will travel further down the air-stream and strike B at $P_2$ (see fig. 1 *a*).

Fig. 1 *a*.




If the upper lid of the box is arranged to slide, the points $P_1$ and $P_2$ may in turn be made to coincide with the slit $S_2$ in B. To detect the ions an insulated plate C, electrostatically shielded and connected to an electrometer, is placed under $S_2$. A small subsidiary field between B and C ensures that the ions arriving at $S_2$ are recorded by the electrometer.

Owing to diffusion and self-repulsion the stream of ions increases in width as it travels across the box. It was therefore necessary to obtain the rate of deflexion of the electrometer needle for various positions in the neighbourhood of P, and to deduce the position of $S_2$ for maximum deflexion graphically. The analysis of spread for different voltages suggested that the effect was mainly due to diffusion, but that self-repulsion became appreciable when the current across the box was large. Diffusion may be cut down by raising the voltage between A and B, thus lessening the time spent by the ions in crossing the box. This, however, lessens the displacement of the ionic stream by the air-current, and cannot therefore be carried beyond a certain limit. Preliminary experiments led us to adopt voltages ranging from 30 to 300 volts across the box and an ionization current sufficiently small to make mutual repulsion negligible.

For maximum resolving power the slits $S_1$ and $S_2$ must be very narrow when, however, the number of ions passing through them is too small for measurement. Since the

resolving power was already limited by diffusion, we have remained satisfied with a width of slit of 4 mm. which was adopted early in the work after a few preliminary experiments.

In order to minimize the effect of eddies near the slit $S_1$ and the loss of ions in passing through it, the slide in its immediate neighbourhood was made thinner than the rest of the box. The lower edges of the slit $S_2$ were bevelled off for the same reasons.

The movement of $S_1$ was obtained by making A in two parts. The main fixed part contained a large rectangular opening, over which was placed a brass slide 48 in. × 7 in. containing the slit at its centre. A good sliding fit between the two parts was ensured by pressure from a number of fairly stout springs. When the air-stream passed through the box, a layer of vaseline around the edges of the slide made any sideway leak of air negligible. Guides were also provided.

The chamber containing the hot filament "*f*" was made of plastic fire-cement, lined with mica. Copper hooks were inserted in opposite walls for supporting the wire horizontally and parallel to the slit. Platinum wire of S.W.G. 44 was used. The bottom of this chamber was a mica sheet, slotted over the slit $S_1$ and cemented to the brass slide; the top of the chamber was a thin aluminium sheet. The walls and top were made airtight, because any leak would have caused a flow of air from the main stream through the chamber.

The electrode C under $S_2$, together with the electrometer, its key and connexions, were electrically shielded. The sensitivity of the electrometer was usually about 70 to 80 cm. per volt.

During an experiment the following voltages were applied:—(a) "*v*" between the aluminium top and the filament "*f*"; (b) "$v_1$" between "*f*" and $S_1$; (c) "V" between A and B; and (d) "$v_2$" between S and C.

*The Air-stream.*—It was of course necessary to use a very steady stream of dry dust-free air. In fig. 1, R is a Keith Blackman rotary blower, rated at 700 revs. per minute, the speed at which it ran most steadily. The air-stream that it furnished to the apparatus was varied by a screw-clip $c_1$ controlling an alternative escape, and by another clip $c_2$ in the main flow. T is a steadying chamber of about 2 c. ft. capacity; "*r*" is a pressure regulator of the type used by Blackwood *; F is an efficient dust-filter.

The speed of the air-stream was measured by reading a

* Blackwood, Phys. Rev. xvi. p. 87 (1920).

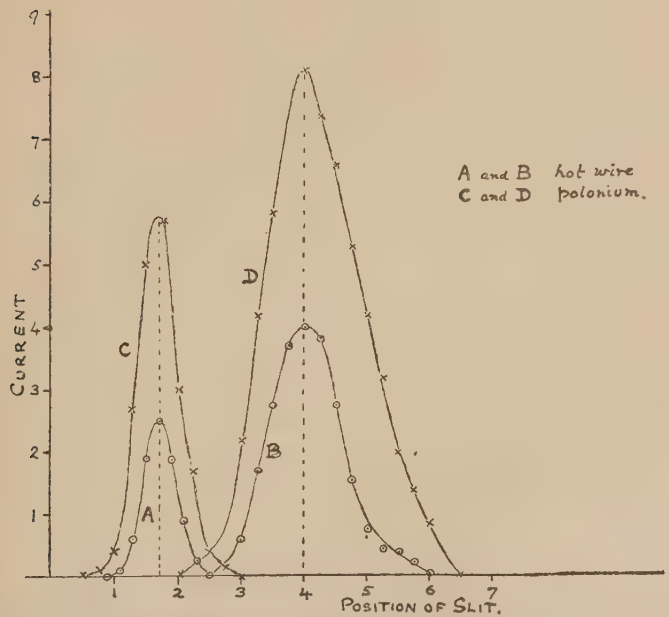
U-tube oil-gauge G placed across the filter, the gauge having previously been calibrated by a gas-meter temporarily inserted in the air-circuit. The readings of flow were usually steady to less than 1 per cent.

$D_1$ is filled with sulphuric acid and $D_2$ with calcium chloride. E is a wooden airtight box which tended by its size and shape to produce even distribution and stream-line flow through the mobility box AB.

### *Experimental Results.*

*Negative Ions.*—Typical results are given in Curves I. The potential differences used in this case were : $r=6$, $r_1=80$, $V=30$, $v_2=6$ volts. The heating current was kept constant

Curves I.




as nearly as possible by means of a microscope focussed on the ammeter needle, and a variable resistance. The air-current varied by less than $\frac{1}{2}$ per cent.

Curve I. A shows the distribution of current at B (due to the hot-wire ions) when no air was flowing, while curve I. B shows the corresponding distribution with the air-current on. It can readily be shown that if "$kX$" is the velocity of the ions in a field X, "$h$" the height of the box, and "$w$" the mean velocity of the stream-line air-flow, then, neglecting

the effect of the sides of the box, which was of considerable width, the displacement of the peak "$l$" is given by

$$l=\frac{hv}{kX}.$$

In other words, when the conditions are kept constant, the displacement is inversely proportional to the mobility of the ions.

The mean value of K deduced from a number of such curves was K=1·71. But since the accuracy of the gas-meter was doubtful at the high speeds used in this case, this number can only be regarded as a rough value. In order to ensure that its approximate agreement with the known value for a normal air ion was not accidental, the hot filament was replaced by a sample of polonium arranged to ionize the air in the chamber, but shielded to prevent the direct entry of rays into the air-stream. The result was the curves I. C and I. D, showing in a striking manner the identity of the mobilities of the ions from the two sources.

The increase in the values of the ordinates of the displaced distribution curve is characteristic of all the curves obtained. It seems reasonable to attribute it to slight eddies in the neighbourhood of the slits, carrying through them ions which would otherwise be caught by the sides of the slits.

A detailed search was then made for ions of lower mobility, the difference of potential "V" being raised to 144 volts for the purpose. The slide was moved 2·5 mm. at a time to a point at which an electrometer deflexion would have indicated a mobility of 0·005 cm./sec. Throughout the whole time, however, the electrometer was perfectly steady. The age of the ions entering the box was increased by reducing the voltage $v$ from 80 to 30, with, however, the same result. This seems to prove conclusively that *only normal ions were present.*

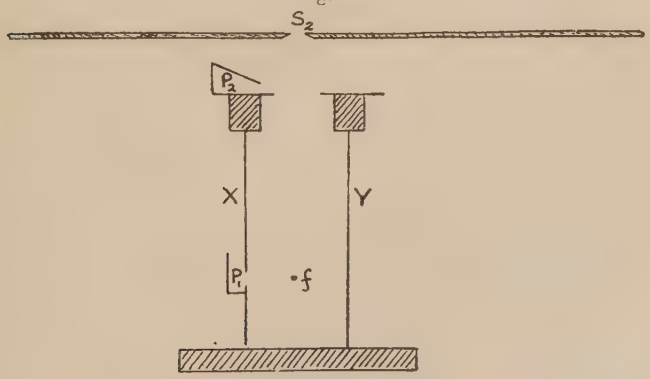
The apparent discrepancy between this result and that of previous investigators receives, however, a simple explanation. If no larger particles are present, the electrons emitted from the hot filament will attach themselves to molecules and become normal ions. In the absence of an electric field they will be carried upwards by the convection current set up by the hot wire. In our experiments the electric field applied was sufficient to reverse their motion and to pull them out of the hot stream down to the slit. Now, if either ions of low mobility or uncharged particles are emitted from the wire as well, these will also be carried upwards; the

former will be pulled down to the box only by very strong fields, fields too strong to be applied conveniently ; the latter will be unaffected by any field. When the normal ions remain with such particles in the same stream, clustering will take place and the mobility of the ions will decrease with time, as McClelland found in his experiments. When the normal ions are rapidly removed downwards from the vicinity of the wire, as in the present work, they will preserve their identity and will alone be observed in the box.

It was felt that some information on the nature of these nuclei might be obtained by inverting the hot filament chamber, placing it under $S_2$, and allowing the nuclei as the result of convection to enter the main air-stream through $S_2$ and to pass across to the electrometer connexion C, now placed above $S_1$. Since, in this case, C had to move with the slide, special spring connexions with the electrometer had to be arranged.

The passage of the convection current across from the slit to the top of the box was clearly demonstrated by supplying some ammonium-chloride fumes to the chamber and watching their deflexion down-stream.

Fig. 2.



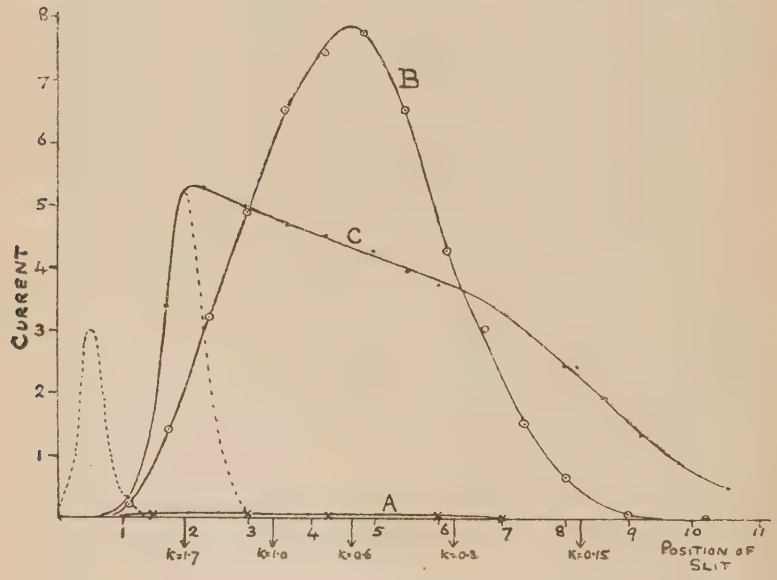

Owing to this convection current, the displacement of the ions by the air-stream was not inversely proportional to their mobility, as in the previous experiments. Some comparative experiments with polonium ions and a convection current from a hot but not incandescent eureka coil gave us an empirical calibration, showing the variation of displacement with mobility for particular values of the air-stream, convection current, and voltage across the box.

Fig. 2 shows the modification of the hot filament chamber which was made. X and Y are parallel plates, 2·8 cm.

apart, between which a potential of 400 volts could be established at will. $P_1$ is a receptacle in which polonium could be placed so that a horizontal beam of $\alpha$-rays would ionize the region around the hot filament $f$. $P_2$ is an alternative receptacle for introducing ions in the same way into the convection stream after it leaves the space between the plates and before it enters the main box through the slit $S_2$.

Three sets of observations were made of the distribution of the ionic stream crossing the box, curves II. showing the results obtained.

Curves II.




Curve II. A.—Filament red hot, with no polonium and no field between X and Y.

Curve II. B.—Filament red hot, with polonium in $P_1$ and no field.

Curve II. C.—Filament red hot, with polonium in $P_2$ and field applied. The dotted curves refer to normal ions with and without the air-current.

These curves are fully explained on the view that accompanying the emission of normal ions there is an emission of

*uncharged* particles in large excess. Thus curve II. A shows only a small current reaching the electrometer, owing to recombination of ions with one another. If, as in case B, a large supply of normal ions is added at the filament, many of the uncharged particles will take up ions which, owing to their consequent decrease in mobility, will recombine far more slowly, and will therefore enter the box in large numbers, as shown in curve II. B. The resolving power of the apparatus does not permit us to say if any particular groups of ions were present, but the smoothness of the curve suggests the existence of a number of ions of all sizes from normal to those of mobility about 0·1, the majority in this particular experiment ranging around a mean value of about 0·6 cm./sec.

It is quite possible that there were also ions of lower mobility; but owing to the eddies which were produced where the convection current struck the top of the box, these escaped detection.

In case C the purpose of the field was to remove all normal ions rapidly from the convection stream. Without any polonium it was then shown that no ions entered the box. Again, the presence of uncharged particles in the convection current was clearly demonstrated by supplying ions to it from $P_2$ just before it enters the box. Curve II. C shows the result. Clearly in this case an appreciable number of normal ions due to the polonium enter the box, while many others attach themselves to the particles which have probably been coagulating as they rise. The result is a big range of mobility from normal to less than 0·1. A smoothed curve is drawn through the points, because a repetition of the experiment showed that there was no special significance in the local variations. We have recently found that in the detection of uncharged particles from hot wires in dry air we have been anticipated by McClelland and McHenry *. In the last section of a paper on nuclei produced in moist air by ultra-violet light and other sources, they show that uncharged nuclei are driven off from metals by heat in air, whether dry or moist. They showed their presence by passing them over uranium oxide when they combined with normal ions and became large ions, as indicated by the high voltage necessary for a saturation current.

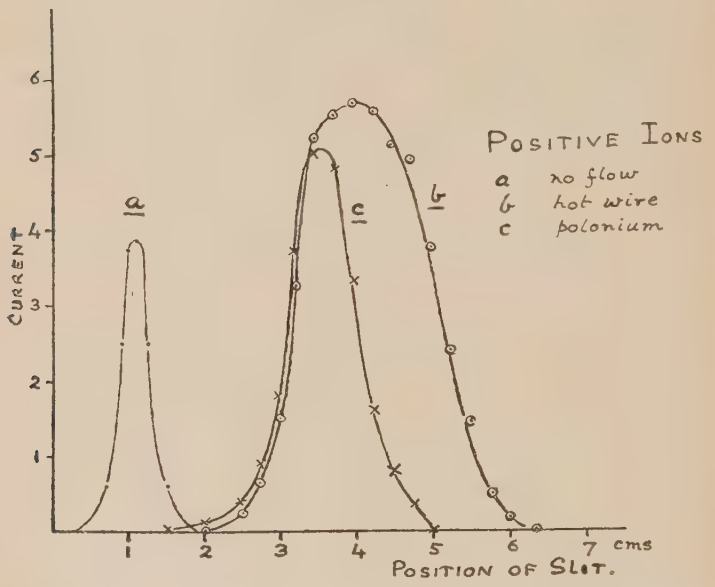
*Positive Ions.*—Similar experiments were carried out with the positive ions emitted from a hot wire. Typical results are shown in curves III. for positive ions pulled *downwards*

* Proc. Royal Dublin Soc. xvi. p. 282 (1921).

out of the convection stream, the notation being the same as that of curves I. for negative ions.

Comparison with curves I. shows that while the negative ions from polonium and from the hot wire are identical, this is not the case for positives. The wide spread of the positive

Curves III.




ions from the hot wire suggests that they consist of a mixture of ions of various sizes ranging round a mean value of mobility of about 1·0 to 1·1 cm./sec.

Attempts were made to analyse this distribution by repeating with different values of $v_1$, but the positive emission from a wire was found to be not steady enough to ensure reliable comparative results.

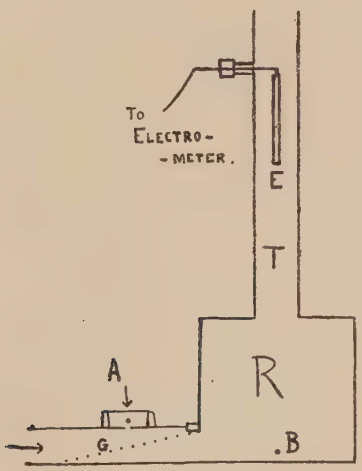
Experiments with the inverted box were also carried out in the same manner as with negative ions with similar conclusions. In fact, the curves obtained are so similar to those in curves II. that it seems unnecessary to reproduce them.

### *The Second Method.*

McClelland's original mobility apparatus was modified to show results which confirmed those obtained above with negative ions. The positive emission was not steady enough

to use it satisfactorily. The arrangement is shown in fig. 3. The source of the ions, either hot wire or polonium, could be placed either in the receptacle A, as in the box method, or in the main stream at B. The electrode E, insulated and connected to the electrometer, was suspended centrally in a long tube T, 7·4 cm. in diameter, the potential of which could be varied. The air-stream, dried and filtered, was driven through a gauze G up the tube T, carrying with it ions from either A or B. The vessel R was inserted to ensure uniform distribution of the ions by turbulence before

Fig. 3.




they entered T. Preliminary experiments with tobacco smoke showed that for the air-speeds used the flow in T near E was stream-line.

Typical results are shown in curves IV., the curves A and B being for the hot wire at A and B respectively. Curve IV. A shows a saturation voltage at about 2·8 volts, which is about the right value for normal negative ions for the dimensions used. Repeating the curve with polonium in A instead of the hot wire gave a curve with the bend at the same point within the limits of experimental error. The absence of any other ions suggested by the apparent horizontal character of curve IV. A beyond the bend was confirmed by taking a series of readings alternating between

10 and 20 volts to eliminate possible fluctuations in air-speed or accumulator voltages. The table shows that the mean values are the same at both voltages.

Curves IV.

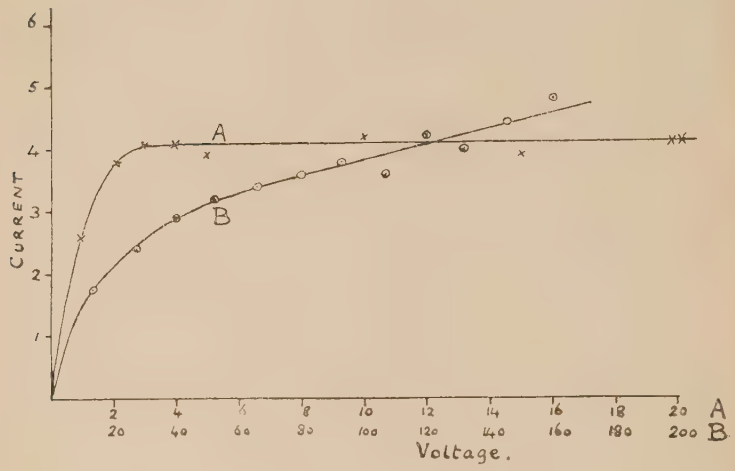



TABLE I.

| Electrometer deflexion in cm. per minute. | |
|---|---|
| 10 volts. | 20 volts. |
| 8·8 | 8·7 |
| 8·0 | 8·0 |
| 7·6 | 8·1 |
| 8·5 | 8·3 |
| 8·5 | 8·8 |
| 8·8 | 9·1 |
| 9·0 | 8·8 |
| 8·8 | 8·6 |
| 8·50 | 8·55 |

Curve IV. B for the wire placed in the air-stream (plotted on a different voltage scale) shows no saturation below 200 volts, which would correspond to a mobility of about 0·005. The general inference to be drawn from the curve, which is convex upwards from an early stage, is that one was dealing with a mixture of mobilities from, say, 0·1 to

less than 0·005. While the curves do not show any evidence of homogeneous groups of ions, it is doubtful whether, if such groups were present, the resolving power was high enough to separate them. These results are in agreement with those of McClelland.

*Discussion and Conclusions.*

The conclusion to be drawn from the above experiments is that the hot filament emits electrons, positive ions, and a copious supply of uncharged particles. When removed from the vicinity of the particles, the electrons attach themselves to molecules and become normal ions of mobility the same as that of negative ions produced by polonium. In the first method the mobility was measured within $\frac{1}{5}$ of a second from birth and in the second method after 5 to 15 seconds with the same results, showing that, removed from nuclei, the "normal" ion retains its identity unchanged with age.

The positive ions are complex. The approximate coincidence of the left-hand side of the curves III. *b* and *c* strongly suggests that positive ions of mobility about 1·4 in air were given off from the hot wire; but there must also have been many ions present having mobilities from 20 to 60 per cent. lower than this. Hütterman * has shown that *in vacuo* a hot wire emits not only gaseous positive ions but positive atoms of the metal, and our curve might be accounted for in this way. It is, however, a little doubtful whether a mobility of the order of 1·1 instead of the normal 1·4 could be that of foreign gaseous ions or of platinum atoms in air. Blanc † has carried out some work which suggests that the mobility of the $CO_2$ ion *measured in air* is the same as that of an air ion. Similar results have been obtained by Wellisch ‡ for ions of methyl iodide in an atmosphere of hydrogen. Again, Franck § arrives at the same conclusion in the case of the positively-charged recoil atoms of thorium D.

If we accept their results, we must conclude that the positive ions are emitted either as small metallic clusters or as atoms, many of which form clusters by the time they reach the box. The clusters, however, must be small compared with those we usually designate as large ions.

* Hütterman, *Ann. d. Physik*, lii. 8, p. 816 (1917).
† Blanc, *Journal de Physique*, vii. p. 825 (1908).
‡ Wellisch, Proc. Roy. Soc. lxxxii. p. 500 (1909).
§ Franck, *Deutsch. Phys. Gesell. Verh.* xi. 19, p. 397 (1909).

The wire when used for positive emission was only at dull red heat; the convection current from it was therefore less than when it was negative. A certain amount of clustering of ions with uncharged nuclei may possibly, therefore, have taken place before they were separated. The emission of the negative ion as an electron with high mobility, together with the greater convection current, would account for the absence of similar clustered ions in the results for negative discharge*.

The uncharged particles are presumably metallic clusters ranging in size from atoms to metallic dust. Left in association with ions they take up charges and become large ions. No doubt they are responsible for the blackening of filament lamps. Removed from ions they coagulate with time like other particulate clouds.

We are indebted to the Colston Research Society of the University of Bristol for a grant in aid of this research.

Physics Department,
University of Bristol.

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## LXIV. *The Valency Bond. Electrovalence and Covalence.* *By* S. H. C. Briggs, *D.Sc.*†

LANGMUIR (Journ. Amer. Chem. Soc. xli. p. 868, 1919) distinguishes between two types of valency known as electrovalence and covalence. When atoms combine by electrovalence a transfer of one or more electrons takes place from the positive to the negative element, and the resulting ions are then held together by the general electrostatic attraction as in potassium chloride $K^{\cdot}Cl'$. When atoms combine by covalence no electrons are transferred,

* Erikson has recently investigated the positive ions from hot platinum in air. An abstract of his work appears in the Physical Review (vol. xxi. p. 720, 1923). He finds that:—"During an interval of the order of 0·30 of a second the initial positive ion changes over into the normal positive ion of mobility 1·36 cm./sec./volt/cm. Since in the initial stage and in the final stage as well, the mobilities are the same as for the positive ion produced in air by the alpha rays from polonium, the conclusion is that the ions are identical . . . . . If the platinum is at a very high temperature and the ions are allowed to remain for a short time in the air which has left the platinum surface, they load up and form heavier ions."

It would, however, be premature to discuss the points of difference between his results and ours before a full account of his work appears.

† Communicated by the Author.

but two or more electrons are shared between the atoms in

$$\begin{matrix} & \mathrm{H} & \\ & \ddot{} & \\ \mathrm{H}:\ddot{\mathrm{C}}: & & \mathrm{H}, \\ & \ddot{} & \\ & \mathrm{H} & \end{matrix}$$

combination, as in methane, in which each hydrogen atom shares two electrons with the carbon atom.

With certain exceptions which are discussed below, electrovalence compounds correspond to strong electrolytes, and covalence compounds to non-electrolytes. Many previous writers have suggested different constitutions for strong electrolytes and non-electrolytes, but have generally regarded the two types of compound as the extremes of a series with an indefinite number of intermediate stages. Langmuir, however, appears to have gone much further than previous writers in the direction of making a clean cut between the two classes, and has thereby done a considerable service to chemical theory, because the idea of two distinct types has attracted much attention and greatly stimulated chemical thought.

There seems to be an increasing tendency on the part of chemists to accept the view that compounds can thus be divided into two distinct and independent classes, but in my opinion the case for *two clearly defined* and *separate* types has not been established. The present paper is therefore devoted to some aspects of this problem.

### 1. *The sharing of electrons.*

Consider a molecule of a strong electrolyte $A^{\cdot}B'$ (an electrovalence compound) formed by the union of an atom of an alkali metal $A$ with the halogen atom $B$, $A$ giving up its solitary valency electron in order to complete the octet round $B$, the atom $A$ thereby becoming a positive ion $A^{\cdot}$, and the atom $B$ a negative ion $B'$.

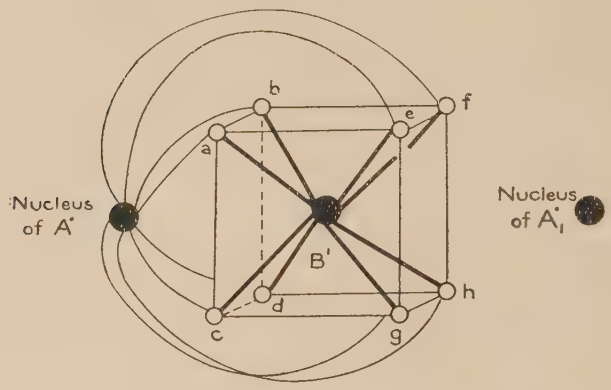
For the sake of simplicity in reasoning, we will adopt the Lewis-Langmuir hypothesis that the eight electrons comprising the completed octet of $B'$ are situated at the corners of a cube, the nucleus of $B$ being at the centre of the cube, and we will make the further assumption that the cube is not distorted in the molecule $A^{\cdot}B'$.

As in previous papers (Trans. Chem. Soc. cxi. p. 253, 1917, cxv. p. 278, 1919; Phil. Mag. xlii. p. 448, 1921), we will adopt the view first put forward by Sir Oliver Lodge ('Nature,' lxx. p. 176, 1904) that the electron and the positive charge when in combination are united by a bundle of a large number of lines of force, so that in a molecule any

given electron or positive charge may be linked up to more than one positive charge or electron respectively.

In the molecule $A^{\cdot}B'$ (fig. 1) we may regard the positive ion $A^{\cdot}$ as a sphere, because the positive charge is situated at the nucleus, and will therefore act on other ions as if it were distributed equally over the surface of a sphere the radius of which is the nearest distance to which a valency electron in the negative ion can approach the nucleus of $A^{\cdot}$.

Fig. 1.




In this diagram the white circles represent electrons and the black circles indicate nuclei. In order to avoid complication, only the nuclei of the positive ions $A^{\cdot}$ and $A^{\cdot}_1$ are shown, all inner shells of electrons being ignored. The negative ion $B'$ is represented by the cube of valency electrons with the nucleus at the centre, no inner shells of electrons being included. The negative ion $B_1'$ of the molecule $A^{\cdot}_1B_1'$ is not shown in the diagram.

In the ion $B'$ we have a kernel with seven positive charges united to eight electrons. Each electron will therefore be linked to the kernel by a bundle of lines of force containing only seven-eighths of the number of lines present in a complete bundle. This will leave one-eighth of a complete bundle to pass from each electron in the octet of $B'$ to the nucleus of $A^{\cdot}$. The bundles of lines of force are represented diagrammatically in fig. 1 by single lines, the thick lines joining the electrons to the nucleus of $B'$ and the thin lines connecting the electrons to the nucleus of $A^{\cdot}$.

We see, therefore, that in the electrovalence compound $A^{\cdot}B'$ the electrons are shared, but they are shared unequally,

whereas in the true covalence compound they are shared equally. Hence it follows that the difference between electrovalence and covalence is only a difference of degree, the electrons being shared equally in covalence compounds and unequally in electrovalence compounds, the more unequal the sharing the greater the polarity of the compound. If this is the case, it is not possible to divide compounds into two sharply-defined classes, as unequal sharing may include any degree of sharing, from approximate equality to almost complete separation of the ions.

The above reasoning still holds good if the cube is distorted or if the electrons are distributed around $B'$ in some other way and not at the corners of a cube, the effect of such other arrangement being that the electrons will not all be shared in exactly the same manner, but taken altogether will still be unequally shared between $A^{\cdot}$ and $B'$.

### 2. *The crystal structure of strong electrolytes.*

Suppose a second molecule $A_1^{\cdot}B_1'$ to be brought up against $A^{\cdot}B'$ so that the positive ion $A_1^{\cdot}$ is between $B_1'$ and the face *efgh* of the cube $B'$. The lines of force from the electrons *e*, *f*, *g*, and *h* will now have a tendency to attach themselves to the nucleus of $A_1^{\cdot}$, since this nucleus is nearer to them than is the nucleus of $A^{\cdot}$. If a number of molecules were thus joined up in a straight line, we should obtain a chain polymeride in which each ion, positive or negative, would be symmetrically placed with regard to the two adjacent negative or positive ions respectively, and although the original individual molecules would still be present, it would not be possible to distinguish them.

Granted further a suitable relation between the linear dimensions of $A^{\cdot}$ and $B'$, it should also be possible to group the molecules in such a way that an ion $A^{\cdot}$ would be adjacent to each of the six faces of the cube $B'$, and similarly each ion $A^{\cdot}$ would be surrounded by six cubes of $B'$. We should thus obtain the simple cubic space lattice in which sodium chloride and most of the alkali halides crystallize.

If we assume as above that the eight electrons around $B'$ are situated at the corners of a cube, then in the simple cubic space lattice each electron of the octet of $B'$ will be symmetrically placed with reference to the three separate ions of $A^{\cdot}$ adjacent to the three cube faces which meet at the corner occupied by that electron. Instead, therefore, of *one* small

bundle of lines of force passing from each electron of $B'$ as in the figure of the simple molecule, the small bundle will now be divided into three parts, each portion going to a different positive ion. The valency bond connecting the ions will now be very diffusely distributed, and it is easy to see why the solid acts as a conductor, because, whereas seven-eighths of the lines of force proceeding from each electron in the octet of $B'$ pass to the nucleus of $B'$, the remainder are divided up between the nuclei of at least three positive ions. Consequently, when the appropriate electrical conditions are applied, $B'$ retains all the valency electrons and the crystal conducts as if it were built up of the ions $A^{\bullet}$ and $B'$.

The crystal structure of a strong electrolyte is often described as a space lattice of positive and negative ions; and this statement is true, in virtue of the electrical conductivity of the crystal. Again, we may also imagine that when a body like potassium chloride crystallizes from aqueous solution, the crystal grows by accretion of individual ions.

As a corollary to the statement that the crystal consists of a space lattice of positive and negative ions, the further conclusion has been drawn that the crystal of a strong electrolyte does not contain molecules. This is clearly a false deduction, because we have seen above that we can derive the crystal structure by a process of *polymerization* of individual molecules, and this is in keeping with experience. As Caven ('Nature,' cviii. p. 210, 1921) has remarked, sodium chloride exists in the form of molecules at *circa* 2000° C. When such a vapour of sodium chloride cools down and solidifies, it can scarcely be expected that each molecule will break up into individual ions before crystallization. The molecules will rather combine with each other, and thus form the crystal of the solid by polymerization as shown above. It therefore follows that the crystal of a strong electrolyte consists of one huge polymerized molecule, the size of which is only limited by the size of the crystal itself.

And although the crystal may be regarded in this way as being built of polymerized molecules, it may equally well be regarded as a space lattice of positive and negative ions. Both points of view are correct, and are mutually complementary, not exclusive.

*N.B.*—Attention may be drawn to the following analogies,

which may serve to illustrate the point of view indicated in this section :—

(1) If a number of couples waltzing in a ball-room were to join hands in a ring so that each gentleman had his partner on his right and another lady on his left, a stranger coming into the room would not be able to sort out the original couples, although they would still be there. In a crystal of sodium chloride formed by condensation of the vapour, the original individual molecules are still present but cannot be identified, although the ions can be distinguished just as the individual dancers could be distinguished in the ring.

(2) A diamond crystal is usually regarded as being built up by the polymerization of carbon atoms. If a more refined method of crystal analysis could be devised which would reveal the actual positions of the electrons just as X-ray analysis discloses the positions of the atoms, such a refined method would indicate that the diamond was built up of electrons and nuclei rather than of atoms.

### 3. *Compounds intermediate between strong electrolytes and non-electrolytes.*

The properties of aluminium chloride as recently investigated by Biltz and Voigt (*Zeitsch. anorg. und allgem. Chemie,* cxxvi. p. 39, 1923) are of considerable interest for the present discussion. In the solid state aluminium chloride is a conductor, although with the low conductivity of *c.* $0{\cdot}3 \times 10^{-6}$ reciprocal ohms at a few degrees below the melting-point as compared with $3 \times 10^{-6}$ for silver nitrate. Just at the melting-point the conductivity of aluminium chloride vanishes, so that according to Biltz and Voigt solid aluminium chloride consists of a space lattice of ions, whereas the melted salt contains molecules. We may equally well suppose that the solid is built up of polymerized molecules, the valency forces being diffusely distributed as a result of the polymerization so that the solid is a conductor because the electrons are unequally shared, whereas in the liquid either single or double molecules are present in which the electrons are equally shared between the chlorine and the aluminium, and the liquid is therefore a non-conductor.

Intermediate between the strong electrolytes and the purely non-polar compounds we have the great majority of the complex salts, most of which have some tendency to dissociation of the complex in solution. Taking the platinichlorides as an example, according to Langmuir we may regard these as electrovalence compounds, the chloride ion being held to the platinum ion by the general electrostatic attraction, or alternatively as covalence compounds in which the platinum atom is surrounded by a disextet of electrons, two of which are shared by the platinum with each chlorine atom. If each pair of electrons is to be saturated they cannot be shared equally, because for this purpose the platinum ion would require six positive charges, whereas it only actually possesses four. It is evident that the distinction between electrovalence and covalence becomes very vague when the theory is applied to complex inorganic compounds.

### 4. *Langmuir's electrovalence formulæ for certain compounds with non-polar properties.*

There are a number of compounds with the general formula $AB_x$ which have the properties of non-polar substances but which Langmuir regards as electrovalence compounds, because when the octets are completed round the $B$ atoms there are either too few or too many electrons to give an octet round $A$ if $A$ shares two electrons with each atom of $B$.

In a former paper (Phil. Mag. xlii. p. 448, 1921) it was shown that octet formation may be regarded as a co-ordination of electrons, using the word co-ordination in the sense in which it is applied in Werner's theory of complex salts. If we adopt this point of view, there does not appear to be any particular reason why a positively-charged atom should be able to share *only* eight electrons with negatively-charged atoms which have completed octets. On the contrary, in compounds of the formula $AB_x$ we should expect $x$ to be 2, 3, 4, or 6, corresponding to the sharing of 4, 6, 8, or 12 electrons respectively. By adopting such electron co-ordination numbers for the atom $A$, the various examples of non-polar compounds to which Langmuir has given electrovalence formulæ become covalence compounds, as might be expected from their general physical and chemical properties.

With electron co-ordination number four we have the metal atoms in such organo-metallic compounds as mercury diethyl and zinc diethyl, $C_2H_5:Zn:C_2H_5$. Such a formula explains the poor conductivity of zinc diethyl compared with the good conductivity of the salt-like sodium ethyl (Hein, *Zeitsch. Electrochem.* xxviii. p. 469, 1922).

The boron atom in boron triethyl provides an example of the electron co-ordination number six. Although boron triethyl is a non-conducting liquid with a low boiling-point, Langmuir gives it an electrovalence formula and explains the peculiarly non-polar properties by suggesting that the field is wholly internal. The best way to ensure such an internal field would be to share two electrons equally between the boron atom and a carbon atom of each of the three groups, as this could be done without setting up strains in the non-polar ethyl radicles, and a purely non-polar molecule would thus be obtained.

Carbon tetrachloride would be written as a covalence compound, the carbon atom having the electron co-ordination number eight, whereas Langmuir prefers an electrovalence formula to harmonize with the electrovalence formulæ given to sulphur hexafluoride etc.

Sulphur hexafluoride is a tasteless and odourless gas, chemically as inert as nitrogen. Langmuir regards it as an electrovalence compound, with the field wholly internal. Sulphuryl fluoride, also a tasteless and odourless gas, is regarded by Langmuir as a covalence compound, because a formula can be given to it by the equation $e=8n-2p$,

the formula being written $\begin{matrix} & & \mathrm{F} & & \\ & & | & & \\ \mathrm{O} & - & \mathrm{S} & - & \mathrm{O} \\ & & | & & \\ & & \mathrm{F} & & \end{matrix}$. It should be remarked, however, that in this formula the sulphur is left with two positive charges and the oxygen atoms have each a free negative charge. This formula suggests properties quite different from those of a tasteless and odourless gas. The difficulty vanishes completely, however, if we give both compounds a covalence formula in which the sulphur atom has an electron co-ordination number twelve, sharing a pair of electrons with each fluorine atom in $SF_6$, and two pairs with each of the oxygen atoms as well as one pair with each fluorine atom in $SO_2F_2$.

### 5. *Acids, bases, and salts.*

Lowry ('Chemistry and Industry,' xlii. p. 43, 1923) has recently suggested that hydrogen differs from other positive elements in that it is able to enter into various stages of combination from true covalence to strongly-marked electrovalence, and adopting Langmuir's view, he further states that this is the reason why there are strong and weak acids, strong and weak bases, but no weak salts.

From the chemists' point of view it is difficult to understand the statement that there are no weak salts, because in the series KCl, $CdCl_2$, $CdI_2$, $HgCl_2$, $Hg(CN)_2$, $WF_6$ we have a gradual diminution in polar properties from the strong electrolyte KCl to the non-polar gaseous $WF_6$. If we accept the view that electrovalence and covalence differ only in degree, the series presents no difficulty, and it is not necessary to introduce special explanations such as Langmuir brings forward, assuming the existence of "strong secondary valence forces" which prevent the electrolytic dissociation of $HgCl_2$ and $Hg(CN)_2$.

The reason why hydrogen forms non-electrolytes so much more readily than other positive elements is doubtless due to the fact that the hydrogen ion is a nucleus only, as suggested by Lowry. Other positive ions, in comparison with the hydrogen nucleus, may be regarded as very large spheres with the positive charge distributed over the surface. The conditions for the formation of non-polar compounds by such positive ions are strictly limited, as explained some years ago (Briggs, Trans. Chem. Soc. cxv. p. 281, 1919), and this is the reason why most salts are strong electrolytes.

### 6. *Lowry's mixed double bonds.*

In a recent paper (Trans. Chem. Soc. cxxiii. p. 822, 1923) Lowry has suggested that the double bond in organic compounds usually acts as if it contained one covalence and one electrovalence, and has shown that this theory can be successfully applied to many branches of organic chemistry. The formula for ethylene $\overset{+}{C}H_2—\overset{-}{C}H_2$ obtained in this manner raises a question of some interest. Polar compounds generally have a tendency to polymerize, and a substance of the formula $\overset{+}{C}H_2—\overset{-}{C}H_2$ might be expected to be a solid at the ordinary temperature rather than a monomolecular gas.

The difficulty can be avoided if Lowry's formula represents an active phase through which every molecule passes, but in which only a small proportion of the molecules exist at any given instant *. Such an active phase might arise by the distortion of the molecule due to thermal agitation or some other cause, two of the shared electrons in Langmuir's formula being taken away from one carbon atom as to leave only a single valency bond. This is shown diagrammatically in fig. 2 *a*, which represents the normal molecule as pictured by Langmuir, and fig. 2 *b*, the distorted molecule corresponding to the formula $\overset{+}{C}H_2—\overset{-}{C}H_2$. The

Fig. 2 *a*.

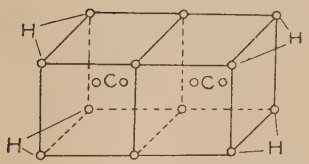
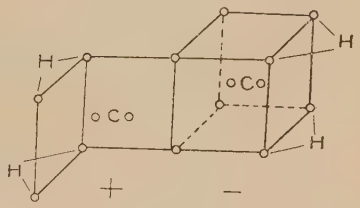



Fig. 2 *b*.




distorted molecule might be expected to swing back at once to the symmetrical form *a*; and it is not necessary to assume that the two internal electrons of the positive carbon atom come out to the surface in order to complete the octet. Similar considerations would apply to benzene, which is a truly non-polar compound according to Sir Joseph Thomson (Phil. Mag. xxvii. p. 764, 1914).

If this view of Lowry's ethylene formula is accepted, it is clear that the difference between electrovalence and covalence is only a question of degree, due to the varying positions of the electrons.

### 7. *The magnetic theory of valency.*

In the preceding sections it has been assumed throughout that the valency forces are purely electrical. It was shown in section 1 that electrons are shared in electrovalence compounds (strong electrolytes), but that they are shared unequally. Since electrons are shared equally in true covalence compounds such as a molecule of oxygen in which both atoms are electrically neutral, it was suggested

* In a more recent paper Lowry has expressed a similar view. (Trans. Chem. Soc. cxxiii. p. 1866.)

that covalence corresponds to equal sharing of electrons and electrovalence to unequal sharing, the difference between electrovalence and covalence being therefore only a difference of degree.

The actual relation between electrovalence and covalence, as these terms are used by Langmuir, does not appear, however, to be quite as simple as this, since Langmuir has given covalence formulæ to the complex ions in co-ordination compounds in which the electrons cannot be shared equally, as shown in section 3 above.

Again, electrovalence compounds are usually regarded as strongly polar, and covalence compounds as non-polar; but instances were given in section 4 in which Langmuir has suggested electrovalence formulæ for non-polar compounds. It was shown, however, that it is possible to give these compounds covalence formulæ by adopting the principle of the co-ordination of electrons.

If the views of Oxley (Proc. Roy. Soc. A, xcviii. p. 264, 1921) and Peirce (Phil. Mag. xlv. p. 317, 1923) and others are accepted, in electrovalence compounds the valency forces are electrostatic, and in covalence compounds the valency is due to magnetic attraction between two electrons, the doublet occurring where electrons are "held in common" in Langmuir's theory of chemical combination. From this point of view there would be an actual difference of kind between electrovalence and covalence. It would then be necessary to explain the gradation in properties from strong electrolytes to non-electrolytes familiar to the chemist.

Do these different degrees of polarity represent different degrees of electrovalence? and, if so, is it possible to have non-polar electrovalence compounds with equal electrostatic sharing of electrons as well as non-polar covalence compounds due to magnetic attraction?

If there are two such types of non-polar compounds, by what tests can they be distinguished? If there are not two distinct types of non-polar compounds, what is the physical interpretation of the properties of weak electrolytes intermediate between strong electrolytes held together by electrostatic forces and non-electrolytes due to magnetic attraction?

The words electrovalence and covalence are coming into general use in chemical literature, and it is highly desirable from the chemist's point of view that a precise physical definition should be given to these terms.

*Addendum.*

The substance of this paper was given in the form of an address to the Priestley Club, Leeds, on March 13th, 1923. The paper was sent in for publication in June 1923, before the discussion on valency at Cambridge, arranged by the Faraday Society.

In a paper published in 1923, Knorr (*Zeitschrift für anorganische und allgemeine Chemie*, cxxix. p. 109) showed that if Bohr's theory is accepted and it is assumed that atoms combine by the sharing of electron *orbits* rather than by the sharing of electrons, then there is no clear distinction between electrovalence and covalence ("Ionenbindung und Atombindung") (see also Fajans, *Naturwissenschaften*, xi. p. 165, 1923). In this connexion it should be observed that "the sharing of electron orbits" and "the co-ordination of electron orbits" may be substituted in the above paper for the "sharing of electrons" and "the co-ordination of electrons" without affecting the general argument.

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## LXV. *An Apparatus for Purification of Radium Emanation.* *By* Victor F. Hess, *Ph.D.**

RADIUM salts are so precious that handling of radium preparations in small, thin-walled glass tubes always involves a certain risk. Since radium itself does not emit any gamma rays of high penetrating power, while the emanation with its successive products gives off alpha, beta, and gamma rays, it is in most cases preferable to use "emanation tubes"—*i. e.* small glass tubes containing emanation instead of radium. The walls of these emanation tubes can be made thin enough to allow the passage of alpha rays †.

Sir William Ramsay and F. Soddy ‡, Sir Ernest Rutherford §, A. Debierne ‖, S. C. Lind ¶, William Duane **, and others have described apparatus by means of

* Communicated by the Author.

† E. Rutherford and T. Royds, Phil. Mag. (6) xvii. p. 281 (1909).

‡ W. Ramsay and F. Soddy, Proc. Roy. Soc. A, lxxiii. p. 346 (1904).

§ E. Rutherford, *Sitz. Ber. Wien. Akad. d. Wiss.* vol. 117. p. 925 (1908); & Phil. Mag. (6) xvi. p. 300 (1908).

‖ A. Debierne, *Compt. Rend.* vol. 148. p. 1264 (1909).

¶ S. C. Lind, *Sitz. Ber. Wien. Akad. d. Wiss.* vol. 120. p. 1709 (1911). Also R. E. Nyswander, S. C. Lind, and R. B. Moore, Astrophys. Journ. liv. p. 292 (1921).

** W. Duane, Physical Review, (2) v. p. 311 (1915); Boston Med. and Surg. Journ. vol. 177. p. 787 (1917).

which it is possible to pump off practically all emanation produced in a given radium solution every day and to remove the gaseous impurities. The purified emanation finally is sealed up in little glass tubes very much smaller than the tubes which contain the equivalent amount of radium in form of highly concentrated salts. All these devices or "emanation apparatus," as they are called commonly, have the advantage that the precious radium solution is permanently kept in a vault, safe from any damage, fire, or theft.

These emanation apparatus are particularly advantageous for hospitals and similar institutions where radium work is done every day. Within the limits of the amount of radium at disposal, the operator can produce tubes of almost any desired strength by subdividing the capillary glass tube in which the purified emanation finally is sealed. One gram of radium in solution gives a daily output of about 160 millicuries of emanation. Pumping off every day, the operator produces out of 1000 mg. of radium about 1020 millicuries per week. In the following week, the tubes of the first week are still strong enough, so that the laboratory or hospital after a short time has a great number of emanation tubes of various strengths at disposal.

In aqueous radium solutions together with emanation a number of other gases are formed continuously by the action of the radiations: large quantities of hydrogen, oxygen, carbon dioxide, chlorine or bromine, and traces of organic vapours which are generated by the action of emanation on stopcock grease. In addition, a very small amount of helium is produced by the radioactive decay.

The apparatus for purification or concentration of emanation are working on the principle of certain chemical reactions and physical effects such as :—

(*a*) Combination of H and O by sparking or by exposure to an incandescent filament.
(*b*) Absorption of water-vapour by $P_2O_5$ or other chemicals.
(*c*) Removal of excessive amounts of hydrogen by oxidation with a heated copper-oxide coil (W. Duane), or
(*d*) Separation of emanation by imbedding the end of the capillary tube in liquid air (liquefaction of emanation).

The principles (*a*), (*b*), and (*c*) are used in Duane's apparatus (*l. c.*) and in a similar improved apparatus of G. Failla * (Memorial Hospital, New York City), who

* 'Archives of Radiology and Electrotherapy' (June 1910).

designed special vacuum stopcocks with graphite instead of vacuum grease.

For continuous use all these apparatus involve certain difficulties. They require skillful, well-trained operators. Whenever a break occurs in an elaborate apparatus, it can be repaired, as a rule, only by a professional glass-blower. Sometimes repairs are impossible, because the glass by the action of the rays becomes brittle and does not seal with fresh glass of the same sort. In order to avoid delays in case of breakage, G. Failla has adopted the principle of using a "twin apparatus" consisting of two identical glass apparatus connected to the same radium solution.

The apparatus which give a high-grade purification, such as Duane's and Failla's, cannot be used efficiently with much less than 500 mg. of radium in solution.

The author intended to construct an apparatus for purification of radium emanation simpler and smaller than these elaborate machines primarily for the use of physical and chemical institutes, for small hospitals, and for the average radium practitioner who cannot afford to buy 500 or 1000 mg. of radium.

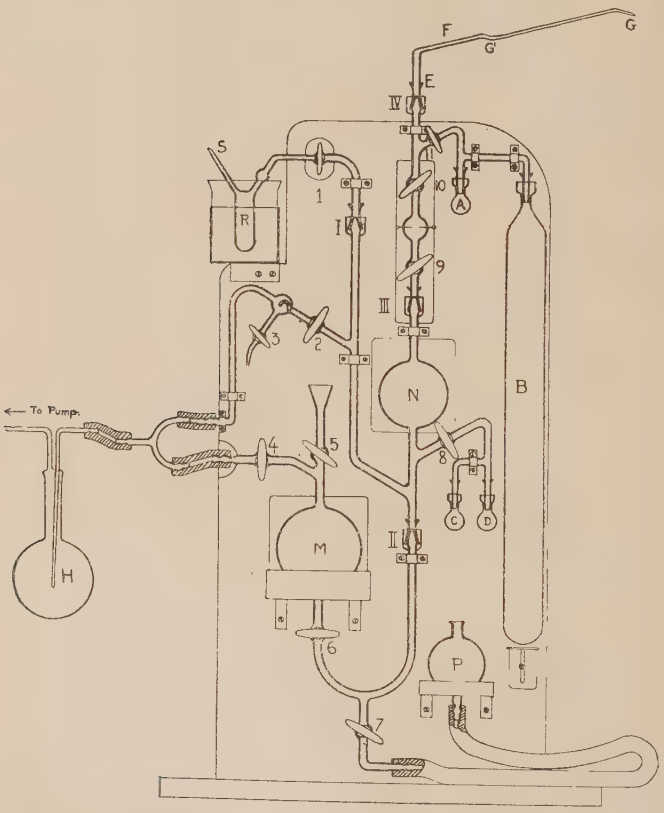
Fig. 1 shows the new apparatus in a vertical section. The heavy lines mark the glass apparatus, which is mounted on a wooden board 70 cm. high and 36 cm. wide. The whole apparatus, together with the radium solution (R), can be kept in a safe cabinet of the usual size The apparatus is made in five parts, which can be detached and re-assembled within half-an-hour. In fig. 1 the joints (mercury-sealed) are marked with I, II, III, and IV. Cleaning of the apparatus by mechanical means (iron wire with cotton wound around) or liquids is therefore very easy. This is important, since all glass apparatus in which mercury comes in contact with emanation are gradually covered with layers of mercury compounds (chloride or bromide). Internal cleaning of Duane's or Failla's apparatus is not possible without cutting glass connexions and resealing, which sometimes causes serious difficulties, as mentioned above.

The new apparatus is constructed in such a way that every joint can be replaced by an exactly fitting spare joint. The radium solution itself is detachable, and its glass joint I (fig. 1) can be made to fit a second apparatus ("twin principle"). It is also possible to use several bulbs with radium solutions in connexion with one apparatus.

The evacuation can be performed by any rotary pump giving a vacuum of at least 0·01 mm. mercury. The

"Cenco-Hyvac" rotary pump (produced by the Central Scientific Co., Chicago), giving a primary vacuum of about 0·001 mm., was found very suitable. An additional device (shown in fig 1 (B) and discussed later) makes it possible to obtain in the apparatus a hundredfold better vacuum without using an additional pump.

Fig. 1.




The apparatus is made of soft glass. The inside part of every stopcock is made of "pyrex" glass. It was found that sticking of these stopcocks never occurred even when very little grease is used.

In general, the use of ground-joints and greased stopcocks was not avoided, as it was found that the volume of foreign gases was not increased perceptibly by the use of grease in these connexions. This seems to be contrary to the

experience of other observers. But in fact the emanation really is in contact but a very short time (about ten minutes) with most of the greased stopcocks and joints (like Nos. 9, 10, III and IV in fig. 1). Therefore the amount of organic vapours liberated by the action of the emanation is practically negligible.

Only one stopcock is in permanent contact with emanation—No. 1 in the figure. If very high purity of emanation is desired, it is well to grease this stopcock with orthophosphoric acid very carefully once a week. The other communications have to be greased with good vacuum grease once a month when used daily. The radium solution (chloride or bromide in distilled water with barium chloride and a few drops of hydrobromic or hydrochloric acid) is filled into R (fig. 1) through S, and this tube immediately afterwards sealed. If not more than 200 mg. of radium are used, the volume of R can be less than 30 c.c. The solution is surrounded by a beaker and a brass cylinder (mounted on the board) for protection.

The apparatus is connected to the vacuum pump by means of the cocks Nos. 2 and 4 (see fig. 1) and two pieces of vacuum rubber hose with a U-shaped tube. H is a trap-flask. Stopcock No. 4 is used to suck the mercury back to its normal level above joint II.

The mercury bulb N has a volume of 360 c.c., while M contains 500 c.c. The small side bulbs A and C contain some pure $P_2O_5$; bulb D some KOH to absorb moisture and carbon dioxide.

Between the stopcocks Nos. 9 and 10 is the explosion chamber. Two platinum wires, leading to a small induction coil fed by two dry cells (3 volts), form a gap of 6 mm. The character of the discharge gives a very good idea about the vacuum reached, and therefore it was found needless to use a McLeod manometer in addition.

The apparatus is filled with mercury in M and the neighbouring tube to just above the joint II. The levelling bulb P and the vacuum hose attached to cock No. 7 must be filled with mercury. Air bubbles have to be driven out carefully.

The apparatus is so tight that within 24 hours no change in the character of the discharge in the explosion chamber (X-ray vacuum, green fluorescence of the glass walls) can be detected.

Before the experiment one or two little pieces of copper oxide in wire form (5 mm. long) are introduced in the end capillary tube at G and G′ (fig. 1), and one of them shaken

down to the end which is slightly bent down. Inside the end-tube in E a granule of molten phosphorus pentoxide is placed for the final purification of the emanation.

The radium solution, immediately after filling, contains some occluded air which has to be removed. This is done by evacuating the whole apparatus : as soon as stopcock No. 1 is turned on, the solution begins to boil. It is necessary to control this boiling by closing the stopcock partly as soon as bubbles begin to spurt up too fast. When the solution has boiled twice for about 30 seconds and the apparatus has been again evacuated till good Röntgen vacuum is reached (indicated by green fluorescence in the explosion chamber) everything is ready for the first experiment.

After a suitable period of accumulation of emanation—for instance, on the next day—the vacuum is tested first and if found satisfactory the air-sack B (fig. 1) is used in the following way to improve the vacuum:—Stopcocks No. 8 and 4 are closed and Nos. 5 and 6 are turned on slowly. The mercury is driven up in N by the atmospheric pressure, and stopped as soon as it reaches the branch immediately below stopcock No. 11. Then this stopcock is closed. Most of the air residues which were in N and the vertical tube are now caught in the large tube B. Then the mercury is sucked back by the rotary pump after closing stopcock No. 5 and opening No. 4. Now the pressure is so low that no visible discharge can pass the spark-gap. Taking into account the ratio of the volume of the capillary tube EFG to the volume of the air-sack B, we find that a vacuum of about 0·00001 mm. mercury is reached.

Now stopcock No. 10 is closed, and No. 1 turned on very slowly until the radium solution begins to boil ; 30–50 seconds' boiling is sufficient. Most of the emanation is now in the explosion chamber and in N. After closing stopcock No. 1, the emanation is pushed up from N into the explosion chamber by admitting air into M through stopcock No. 5. As soon as the mercury has filled N and touches the lower part of the stopcock No 9 this cock and No. 5 are closed, and the mercury sucked back by the rotary pump till the normal level above joint No. II is reached. Now the solution is boiled a second time by opening stopcock No. 1 for another 30 seconds. By this procedure the last traces of emanation are drawn into the bulb N. After closing No. 1 again, these traces of emanation, together with the foreign gases, are pushed up into the explosion chamber until this is filled with mercury to its lower third.

The gases mixed with emanation contain much hydrogen and oxygen. A single spark of the induction coil between the electrodes causes a bright flash and combination of hydrogen with the equivalent amount of oxygen to water, which is largely deposited on the walls of the explosion chamber.

Now stopcock No. 10 is opened (No. 11 remains closed), and by slowly turning cock No. 6 the mercury rises above the stopcock No. 10, leaving the water behind in the explosion chamber. As soon as the mercury reaches the joint No. IV, its further movement is stopped by shutting off cock No. 6. Now we have the emanation mixed with the excess of hydrogen, $CO_2$, water-vapour, helium, and traces of organic vapours. Hydrogen is removed by heating the tiny copper-oxide wires at G and G′ subsequently from outside by a very small pointed gas flame. It is sufficient to heat these copper-oxide wires to dull red heat for about 2 minutes, in order to reduce the hydrogen. The water-vapour is absorbed by the granule of $P_2O_5$ within the tube near E. Carbon dioxide can be removed by using a small granule of KOH within the end-tube at E in addition. But ordinarily this was found unnecessary. After heating, the gases are allowed to be in contact with the chemicals for 5 minutes. Immediately after, the stopcock No. 6 is opened, and the mercury climbs up towards the end of the capillary tube G. In order to have the emanation tube free from copper oxide, the pointed flame is applied at the very end of the tube until the glass collapses, and is drawn off together with the copper-oxide wire sealed within.

When working with 100 mgs. of radium in solution every day, the residual gases have a volume of about 30 cubic millimetres with 15 millicuries of emanation within, at a pressure of one-fifth of an atmosphere.

Before sealing we can obtain further reduction of the volume by the use of the levelling bulb P (fig. 1), closing cock No. 6 and opening No. 7. It is not advisable, however, to lift P above cock No. 10, because in sealing off the end-tube the pressure inside is naturally increased, and a perforation of the heated thin-walled tube is possible.

The final concentration in the end-tube is about one millicurie of emanation per cubic millimetre. This is sufficient for most purposes.

Sealing off the end-tube is very easy: the tube is held with a forceps, and drawn off as soon as it collapses at the point where the flame is applied immediately above the level of the mercury.

The makers of the apparatus provide 20–40 end-tubes

(like EFGG') fitting to the same joint (No. IV in the figure), so that the apparatus can be operated about one year before any replacement of capillary tubes is necessary. New capillary end-tubes can be drawn out by any glass blower from the bent end E (see fig. 1). Thus the 20 or 40 upper tubes EFG can be used for many years.

In case the purification process as described above is not sufficient for special experiments (for instance, spectral analysis), the liquid-air method can be applied in addition to the method described above, using the same apparatus.

In this case the capillary end of the tube is bent down vertically, and immersed in a small Dewar beaker containing liquid air. The mercury in EF is drawn back to E. A vertical side-tube, provided with a stopcock just above E, enables one to pump off all residual gases while the emanation in the end capillary tube is in the liquid state. Then the stopcock above E is closed, the liquid air removed, and the mercury pushed up towards the very end. This method gives the highest purification.

Ordinarily the concentration of 1 millicurie per cubic millimetre in the end-tube will suffice for physical, chemical, and medical application of radium emanation.

Experiments with this apparatus were continued over a period of one year. The actual amount of emanation in the small capillary tubes was in the average 93 per cent. of the total amount accumulated in the solution in a known period.

The apparatus is made by the U. S. Radium Corporation, New York and Orange, N. J., U. S. A.

I am much obliged to Dr. Edwin D. Leman, Chief Chemist of this firm, for many suggestions and valuable assistance in the course of the experiments.

## *Summary.*

An apparatus is described which gives quick and efficient purification of radium emanation from foreign gases such as hydrogen, oxygen, carbon dioxide, etc., which are mixed with it in radium solutions. The process is based on a combination of known chemical reactions: the equivalent amounts of hydrogen and oxygen are recombined by the electric spark; water-vapour and carbon dioxide are absorbed.

The final purification is done by heating a small piece of

copper-oxide wire in the capillary tube from outside, thus reducing the excess of hydrogen.

The apparatus is small enough to be kept in a safe together with the radium solution attached to it. Only one automatic vacuum pump is used. A special device enables one to increase the vacuum given by the pump about a hundred times. The apparatus is detachable, and can be cleaned inside without cutting any glass connexions. The process of purification of emanation takes about 15 minutes, and gives a final concentration of approximately one millicurie per cubic millimetre. Whenever higher concentration is required, liquid air has to be used in addition. The apparatus can be used with solutions containing from 50 milligrams of radium upwards.

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## LXVI. *The Distribution of Colloidal Particles.*

*By* E. F. Burton, *B.A., Ph.D., and* J. E. Currie, *M.A.**

THE problem of the distribution of colloidal particles was first brought into prominence by the work of Perrin †, which showed that for regions very near the surface of a given volume of solution the law of distribution of the particles is analogous to that regulating the distribution of molecules of gas in the atmosphere. Although the original experiments were carried out for distances up to only one-tenth of a millimetre, the impression that it holds for all distances has got abroad ‡.

Theoretical considerations § show that the law cannot hold for distances even of the order of a few centimetres. Actual experiments by Porter and Hedges ‖ and by one of us § have shown that the distribution is uniform to within an exceedingly short distance from the surface of the solution.

In the paper referred to above § one type of the experiments described consisted in letting a sample of colloidal solution stand in a vertical tube for some two months, after which the concentrations at different layers were measured. In private correspondence with various workers, criticism of this experiment was offered on account of the fact that

* Communicated by the Authors.

† Perrin, 'Atoms,' tr. by Hammick (Constable) (1916).

‡ See Svedberg, 'Colloid Chemistry' (Chem. Cat. Co., 1924), pp. 96–102.

§ Burton & Bishop, Proc. Roy. Soc. A, vol. c. p. 414 (1922).

‖ Porter & Hedges, Trans. Faraday Soc. vol. xviii. pt. 1, Oct. 1922.

rigid precautions were not taken to protect the tubes during the two months from changes of temperature and from light.

*Apparatus.*

In the following paper the record is given of similar experiments in which more elaborate care as to the protection of the tubes was taken. Four tubes (as illustrated in fig. 1)

Fig. 1.

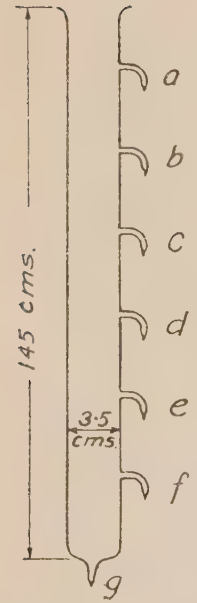
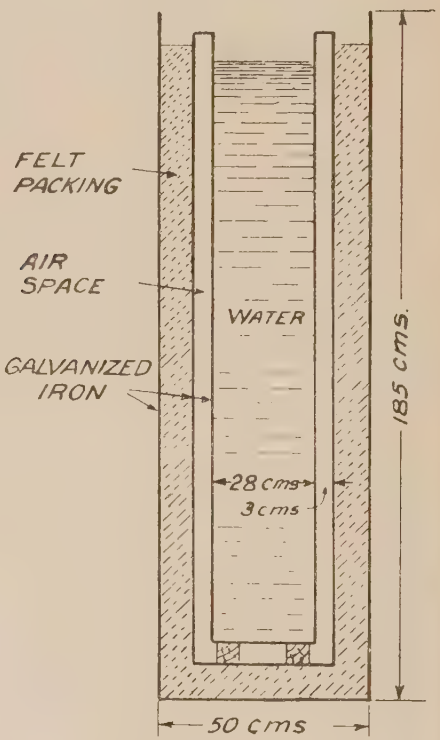



Fig. 2.




were filled respectively with samples of the following solutions: gamboge, arsenious sulphide, copper (Bredig), and silver (Bredig). All of the tubes were suspended so as to be immersed almost to the top in water contained in a large thermostat which was protected from external temperature changes by an air-gap and a space filled with felt (fig. 2). The thermostat was provided with a stirring paddle which

was used from time to time. The tubes were left in this water-bath for a period of four months, during which time there were no abrupt changes in temperature of the water; during the period the temperature of the room gradually changed, due to the starting of the heating system in the building, through about 7° C., and caused a slow change in the temperature of the water of that amount. However, there were no abrupt changes in temperature which would give rise to convection currents. The tubes were kept in darkness up to the time samples were tested.

The samples were drawn off by breaking the points *a*, *b*, *c*, *d*, *e*, *f*, *g* as the tube was raised from the water. In every case the small amount of sediment in the ends of *a*, *b*, *c*, etc. was allowed to run off before the sample was taken.

### *Experimental Results.*

In the use of each of the above colloidal solutions each of the seven samples was treated as follows:—

*a*. Two independent determinations of the concentrations were made.

*b*. Tests were made of the electrical conductivity of the sample, the electrical mobility of the particles, and counts were made of the number of particles per c.c.

With regard to those tests made under (*b*), it would be a waste of space to record all the individual determinations of the various quantities; but with each of the solutions, there was no indication of any change in any of these measured quantities for samples taken from various heights.

In Table I. there are recorded the results of the determinations of concentrations.

TABLE I.

| No. of Layer. | Average distance from top. | Gamboge (mgms. per 50 c.c.). | Arsenious Sulphide (mgms. per 50 c.c.). | Copper (mgms. per 50 c.c.). | Silver (mgms. per 50 c.c.). |
|---|---|---|---|---|---|
| I. | 8·5 cms. | 25·7 | 106·4 | 3·9 | 3·3 |
| II. | 27·5 ,, | 26·7 | 109·5 | 4·3 | 3·9 |
| III. | 48·5 ,, | 26·8 | 104·9 | 4·3 | 3·1 |
| IV. | 69·5 ,, | 26·5 | 105·4 | 4·2 | 3·6 |
| V. | 90·5 ,, | 27·2 | 108·0 | 4·4 | 3·5 |
| VI. | 111·5 ,, | 26·0 | 106·9 | 4·3 | 3·5 |
| VII. | 132·5 ,, | 25·6 | 105·5 | 4·4 | 3·3 |

From these results there seems to be little room for doubt that the particles in these solutions are uniformly distributed and that this distribution is regulated by some mutual action of the particles. In spite of what has been written to the contrary, the possession of like electrical charges seems to offer the most straightforward explanation. It is usually assumed that the existence of the so-called Helmholtz layer leaves the combination, particle plus Helmholtz layers, as an electrically neutral entity. However, the rational view of the Helmholtz double layer, in view of the accepted theory of electrolytic dissociation, is that close up to the particle (or on its surface) is a layer of ions of one sign, while scattered about in a volume outside the particle is an atmosphere of liquid containing ions of both signs, but with those of sign opposite to the charge on the particle in greater concentration than those of the other sign. This might result in the particle having an effective charge of one sign which might easily be the source of mutual repulsion between the particles.

## LXVII. *On a Diffusion Theory of Comets.* *By* Heinrich Mache, *Ph.D., Professor of Physics at the Technical High School, Vienna* *.

If we introduce a bead of easily fusible glass (O) a few millimetres above the tip of the inner cone (K) of the flame of a Bunsen burner, a sharply-defined yellow space (*ss'*) of luminous sodium vapour is formed in the current of gas which is ascending vertically with large velocity at that point. This space envelops the bead, and broadens out in the higher parts of the flame, as seen in fig. 1. Provided the gas-pressure is not too large, it can readily be calculated that the "critical velocity" (Reynolds) will not be exceeded even in these parts of the flame, so that the flow remains laminar, and the sodium vapour developed from the bead is driven into the hot gas solely under the influence of diffusion. The fact that the vapour extends beneath the bead in the direction OA is proof of the high values of the coefficient of diffusion assumed at high temperatures, and at this point diffusion must be able to more than counterbalance the upward flow.

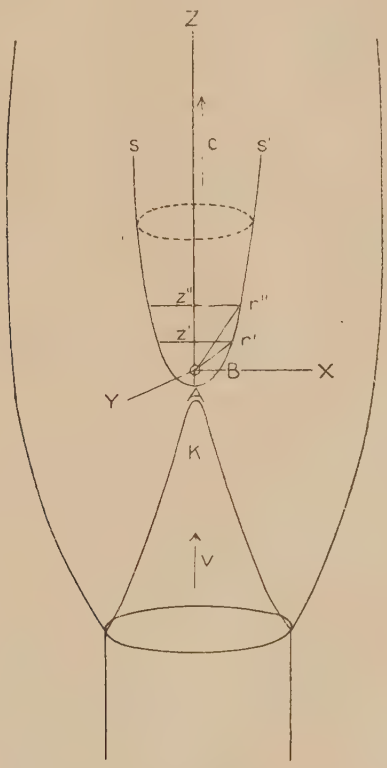
H. A. Wilson † has shown how the coefficient of diffusion

* Communicated by the Author.

† Phil. Mag. xxiv. p. 118 (1912); *cf.* also Proc. Camb. Phil. Soc. xii. p. 406 (1904).

of sodium vapour in the gas of the flame can be determined from measurements of the luminous figure ascending from the glass bead. In § 1 his theory of the phenomenon will be briefly developed, and extended as far as seems necessary in view of the application in § 2.

Fig. 1.




We shall assume that in the space with which we are concerned the flow of gas is everywhere parallel to the axis. This assumption is valid when we restrict ourselves to the central part of the flame above the cone, and can be tested by mixing particles of carbon with the gas, these becoming luminous in passing the cone of combustion and following the lines of flow of the gas. Our second assumption might appear more open to doubt. We shall assume that the same density of vapour exists everywhere along the boundary of the luminous space. In any case, the boundary is sufficiently sharp to enable us to assume that the density gradient at the

limit of visibility is still very large, particularly when we remember that the brightness increases slowly with the density of the vapour and the thickness of the radiating layer *. The limit of visibility must then also represent a surface of almost uniform vapour density.

§ 1. In the theory of the conduction of heat we find an analogous problem to every problem in diffusion ; and for this reason it will be advisable to deal first with the problem in the conduction of heat which is analogous to our present problem.

We suppose a medium flowing with constant velocity $c$ in, say, the direction of the positive $z$-axis. Furthermore, we shall suppose that a source of heat of invariable intensity is acting permanently at a definite point in the medium, this point being at rest as compared with the medium. For the purpose of simplicity let us consider this point to be situated at the origin of the stationary system of coordinates. In the course of time a stationary state would be established, and we have to calculate the form of the isothermal surfaces for this stationary state. In reality this requires the solution of the differential equation :

$$k^2\left(\frac{\partial^2\vartheta}{\partial x^2}+\frac{\partial^2\vartheta}{\partial y^2}+\frac{\partial^2\vartheta}{\partial z^2}\right)-c\frac{\partial\vartheta}{\partial z}=0.$$

Now we can reduce our present problem of heat conduction in the moving body to one in a stationary body, by imagining the permanent source of heat which is actually acting at the origin to be replaced by sources of heat that act instantaneously at every point of the $z$-axis at different times. Each of these instantaneous sources of heat determines a distribution of temperature in the conducting medium, which is readily calculable for a definite time, and by summation we obtain the solution of our problem.

In a stationary medium we have the equation

$$\frac{\partial\vartheta}{\partial t}=k^2\left(\frac{\partial^2\vartheta}{\partial x^2}+\frac{\partial^2\vartheta}{\partial y^2}+\frac{\partial^2\vartheta}{\partial z^2}\right),$$

of which the following expression is a solution :

$$\vartheta=\frac{C}{t^{3/2}}\cdot e^{-\frac{x^2+y^2+z^2}{4k^2t}},$$

or, transforming the coordinates, we have

$$\vartheta=\frac{C}{t^{3/2}}\cdot e^{-\frac{(x-\xi)^2+(y-\eta)^2+(z-\zeta)^2}{4k^2t}}.$$

* Gouy, *Ann. de chim. et de phys.* (5) xviii. p. 1 (1879).

For a medium extending in all directions, this expression gives the existing temperature at any place $x, y, z$, at any time $t$, if a definite amount of heat has been instantaneously introduced at the position $\xi, \eta, \zeta$ at the time $t=0$. The constant C is proportional to the instantaneous quantity of heat introduced.

Let us now consider a point in the medium on the $z$-axis, and at a distance $\zeta$ from the origin. As it passed the origin, heat was instantaneously introduced into this point, and the resulting distribution of temperature in the medium can be calculated from the above by putting $\xi=\eta=0$, and $\zeta=ct$. This gives

$$\vartheta = \frac{C}{t^{3/2}} \cdot e^{-\frac{r^2+y^2+(z-\zeta)^2}{4k^2t}} = \frac{C}{t^{3/2}} \cdot e^{-\frac{r^2-2z\zeta+\zeta^2}{4k^2t}}$$

$$= \frac{C}{t^{3/2}} \cdot e^{\frac{cz}{2k^2}} \cdot e^{-\frac{r^2}{4k^2t}-\frac{c^2t}{4k^2}}.$$

If we integrate this from $t=0$ to $t=\infty$, we obtain the solution of the problem, at first in the form:

$$\vartheta = Ce^{\frac{cz}{2k^2}} \int_0^\infty e^{-\frac{r^2}{4k^2t}-\frac{c^2t}{4k^2}} \cdot \frac{dt}{t^{3/2}} = -2Ce^{\frac{z}{2k^2}} \int_0^\infty e^{-\frac{r^2}{4k^2t}-\frac{c^2t}{4k^2}} \cdot d\left(\frac{1}{\sqrt{t}}\right).$$

By the substitution of $\frac{1}{\sqrt{t}}=x$, we arrive at a known integral, namely,

$$\int_0^\infty e^{-p^2x^2-\frac{q^2}{x^2}} \cdot dx = \frac{\sqrt{\pi}}{2p} e^{-2pq}.$$

We thus have:

$$-\int_0^\infty e^{-\frac{r^2}{4k^2t}-\frac{c^2t}{4k^2}} \cdot d\left(\frac{1}{\sqrt{t}}\right) = \int_0^\infty e^{-\frac{r^2x^2}{4k^2}-\frac{c^2}{4k^2x^2}} \cdot dx = \frac{k\sqrt{\pi}}{r} \cdot e^{-\frac{cr}{2k^2}},$$

and finally, if for brevity we set the constant magnitude $2Ck\sqrt{\pi}=A$,

$$\vartheta = 2Ck\sqrt{\pi} \cdot \frac{1}{r} \cdot e^{\frac{cz}{2k^2}} \cdot e^{-\frac{cr}{2k^2}} = \frac{A}{r} \cdot e^{\frac{c}{2k^2}(z-r)}.$$

The isothermal surfaces are thus surfaces of rotation about the $z$-axis, since a definite temperature corresponds to every pair of values of $z$ and $r$.

The following results are obtained from the discussion of the final equation

$$\vartheta = \frac{A}{r} \cdot e^{\frac{c}{2k^2}(z-r)} \quad \ldots\ldots\ldots \quad (1)$$

At the origin ($r=0$), $\vartheta=\infty$ ;

along the positive $z$-axis ($z=r$), $\vartheta=\frac{A}{r}$;

along the negative $z$-axis ($-z=r$), $\vartheta=\frac{A}{r} \cdot e^{-\frac{c}{k^2}\cdot r}$; and

in the $xy$-plane ($z=0$), $\vartheta=\frac{A}{r} \cdot e^{-\frac{c}{2k^2}\cdot r}$.

If in the plane $z=z'$, which is parallel to the $xy$-plane, a definite temperature exists at the distance $r=r'$ from the origin, and the same temperature in the plane $z=z''$ at the distance $r=r''$, it follows from

$$\frac{A}{r'} \cdot e^{\frac{c}{2k^2}(z'-r')} = \frac{A}{r''} \cdot e^{\frac{c}{2k^2}(z''-r'')}$$

that

$$k^2 = \frac{c}{2} \cdot \frac{(z''-z')-(r''-r')}{\log \frac{r''}{r'}} \quad \ldots\ldots \quad (2)$$

If we seek for points of equal temperature along the negative $z$-axis and in the $xy$-plane, and find them at the distances $r_1$ and $r_2$ from the origin (*e. g.* in the points A and B), we then have

$$\frac{r_2}{r_1} = e^{\frac{c}{k^2}\left(r_1 - \frac{r_2}{2}\right)}$$

and

$$k^2 = c \cdot \frac{r_1 - \frac{r_2}{2}}{\log \frac{r_2}{r_1}} \quad \ldots\ldots\ldots \quad (3)$$

If $k^2$ is small and $c$ is large, the values of $(z''-z')-(r''-r')$ and $\left(r_1-\frac{r_2}{2}\right)$ approach zero, or $(r''-z'')=(r'-z')=\text{const.}$ and $r_2=2r_1$, *i. e.* the isothermal surface approximates to the form of a paraboloid of rotation, the focus of which lies at the origin, and of which the parameter converges towards zero for $c=\infty$. The point of equal temperature lies at

infinity along the positive $z$-axis. If the velocity of flow diminishes, the distance of this point becomes finite, and, provided C remains the same, the lower part of the surface surrounding the origin becomes broader. Finally, for $c=0$, we have $r_1=r_2$, and the isothermal surface becomes a sphere.

The application of these considerations to the present phenomenon of diffusion is obvious. The isothermal surfaces correspond to surfaces of equal partial pressure or of equal density, and from what has been said above, equation (1) is nothing else than the equation of the surface which encloses the sodium vapour developed from the glass bead. The shape of this surface varies according to the velocity of flow of the gas. Could we reduce the velocity to zero, then the surfaces of equal density would be spheres surrounding the bead. The limit of visibility would be distant and badly defined, corresponding to the low density gradient at the boundary. If, on the contrary, the velocity of flow were very great, the surface would take the form of a paraboloid of rotation, with the bead at its focus and with a well-defined boundary, especially in those parts near the bead which are advancing against the flow of the gas and where the density gradient at the limit of visibility attains very high values. The edges of the luminous figure beyond the bead are, however, more and more diffuse, and in the direction of the positive $z$-axis the figure extends theoretically to infinity. Between these two limits there exist all the forms between sphere and paraboloid, each of these forms corresponding to a certain value of the velocity of flow, although, of course, not all of them can actually be observed in the flame of a Bunsen burner, since the flame strikes back into the tube if the velocity sinks below a certain fairly high value.

We shall now give a calculation of the density gradient at each point of the surface of the luminous space, this gradient, taken normal to the surface, being a measure of the definiteness of the limit of visibility. We have, generally,

$$\frac{\partial\vartheta}{\partial n}=\sqrt{\left(\frac{\partial\vartheta}{\partial r}\right)^2+2\frac{\partial\vartheta}{\partial r}\frac{\partial\vartheta}{\partial z}\frac{z}{r}+\left(\frac{\partial\vartheta}{\partial z}\right)^2}.$$

By means of equation (1) we obtain, putting $\frac{c}{2k^2}=\mathrm{B}$,

$$\frac{\partial\vartheta}{\partial n}=-\frac{\mathrm{A}}{r^2}e^{\mathrm{B}(z-r)}\sqrt{1-2\mathrm{B}(1+\mathrm{B}r)(z-r)}.$$

On the surface, $\vartheta$ has a constant value K. Hence in the direction of the positive $z$-axis ($z=r$),

$$\frac{\partial\vartheta}{\partial n}=-\frac{A}{r^2}=-\frac{K}{r},$$

and in the direction of the negative $z$-axis ($-z=r$),

$$\frac{\partial\vartheta}{\partial n}=-\frac{A}{r^2}e^{-2Br}(1+2Br)=-\frac{K}{r}(1+2Br).$$

In the $xy$-plane ($z=0$),

$$\frac{\partial\vartheta}{\partial n}=-\frac{A}{r^2}e^{Br}\sqrt{1+2Br+2B^2r^2}=-\frac{K}{r}\sqrt{1+2Br+2B^2r^2}.$$

From this we can deduce that the distinctness of the edges and the definiteness of the limit of visibility are greatest in the parts of the surface nearest the bead, and that they diminish with the distance from it.

The preceding theory was developed by the present writer, and a set of experiments carried out without knowledge of the previous work of H. A. Wilson. By using formula (2) and measuring the velocity of flow of the flame gases above the cone by a method due to Andrade*, values of $k^2$ were obtained which agree very well with those given by Wilson. Becker †, however, disputes the accuracy of this method, and points out that measurements by Jessel and later by himself and Laub ‡, carried out by a photometric method, gave much smaller values (for sodium vapour 1·0 against 12 cm.²/sec.). It cannot be denied that there exists an uncertainty in the judgment of the light boundary of the luminous figure, and with velocities of flow as are rendered necessary to keep the flame from striking back into the tube, and for values of $k^2<5$ cm.²/sec. the deviations from the paraboloid form are already so small that the measurements become very uncertain. But for values as high as 12 or even 20 cm.²/sec. (in coal-gas-air flames of highest temperature), one can measure mean deviations from the paraboloid in quite a sure way. So the discrepancy remains to be explained.

§ 2. Anyone who observes the phenomenon investigated above will be struck by the similarity it bears to the appearance

* *Ann. d. Phys.* xxxvii. p. 380 (1912).
† Phil. Mag. xxiv. p. 707 (1912).
‡ Heidelberg, *Akad. Ber.* (1911).

of a comet in the neighbourhood of the sun. However doubtful it may seem in general to deduce innate relations from similarity, it is perhaps permissible briefly to indicate that this similarity might be more than simply a formal one.

The nucleus of a comet contains carbon, and it has been shown by spectral analysis that, in consequence of heating by the sun's rays, hydrides of carbon and carbon monoxide are developed from this carbon in the immediate neighbourhood of the sun, and sometimes also sodium- and iron-vapour. But according to the work of Schwarzschild * and of Debye † it is impossible, leaving aside for the moment the case of resonance, that light-pressure exceeds the attraction of the sun for particles of such small diameter as molecules or atoms, even if they be assumed to be totally reflecting. On the contrary, radiation pressure is of negligible magnitude for particles of diameter so much smaller than the wave-lengths in which the sun emits its energy, and this in consequence of the diffraction of the light. In order to cope with this difficulty, it is well known that Arrhenius's theory of comets, which is based on radiation pressure, assumes that the gases ascending from the nucleus condense, and that it is the larger particles formed in this way which are acted on by light-pressure and which form the tail of the comet. But in this case it is very difficult to understand why in the comet's tail often the same characteristic *gas spectrum* is observed as is noted in the neighbourhood of the nucleus.

However, quite recently, Megh Nad Saha ‡ has developed very remarkable ideas about the gases which are raised to immense heights in the solar atmosphere, and this work seems to make it clear why, in the first place, the elements are by no means arranged according to their weights in the atmosphere of the sun. From amongst the known elements, calcium is elevated to the greatest height, in spite of its atomic weight, whilst on the other hand, light elements like boron and nitrogen are entirely absent in the solar spectrum. Saha explains this as due to the calcium atoms being strongly influenced by the light-pressure of the sun, in spite of their smallness, since at these high temperatures and low pressures the calcium becomes ionized by the emission of an electron, and is then rendered luminous by the solar radiation owing to resonance excitation, particularly when the wave-length

* Schwarzschild, *Sitzgsber. d. Akad. zu München,* xxxi. p. 293 (1901).
† Debye, *Ann. d. Phys.* xxx. p. 57 (1909).
‡ Saha, Phil. Mag. xl. p. 809 (1920).

corresponding to resonance lies in the region of the maximum of radiation of the sun. As a matter of fact, Schwarzschild's calculations refer to small reflecting spheres, and an absorption of radiation such as occurs in the case of resonance can give rise to a preponderance of light-pressure over gravitation even with particles of atomic magnitude, as has been noted previously by FitzGerald, Lebedew, and Debye.

Is it not plausible to assume that there is also gas in the sun's atmosphere which, for the same reason, is acted upon by light-pressure with such great intensity that the gas permanently leaves the sun? The green line ascribed to the hypothetical element coronium can be observed up to a height of 20 minutes from the edge of the sun, and the corona attains even to a distances of 6° to 7°, or several times the diameter of the sun. Pringsheim * has already remarked that in the case of the spectrum of the corona we might possibly be dealing with the fluorescence spectrum of a gas ; and in support of this he mentions the "washed out" nature of the main line in the inner corona, and in the case of the outer corona the appearance of the continuous spectrum, which Lockyer describes as being crossed by numerous emission bands. From what we know about the fluorescence radiation of gases we may be concerned here with one and the same gas in the inner and outer corona, which is differently excited under different conditions (temperature, and admixture of foreign gases). Moreover, according to Saha's theory it is not necessary that this coronal gas should be particularly light ; it need only be capable of resonance in the part of the solar spectrum which is rich in energy.

Whatever views we may hold as to the question of the limits of an atmosphere, it must certainly be admitted that a gas that has once been raised to such enormous heights by radiation pressure can also permanently leave the sun, for if the light-pressure is greater than the solar attraction it will remain greater, since both magnitudes and hence also their difference diminish with the square of the distance from the sun. Of course we are dealing here with extremely attenuated gas, the pressure of which, even in the corona, may lie far below that which can be obtained at present with the best vacuum pumps. With increasing distance from the sun this degree of attenuation will diminish still further, so that the motion of the planets will not be influenced in the least. Even Seeliger's theory of the zodiacal light, which

* Pringsheim, 'Physik der Sonne,' p. 319. Leipzig (Teubner), 1910.

attempts to explain the empirical terms in the motion of the inner planets, would permit a mean density of the zodiacal cloud such as could be attained by our vacuum pumps. Nevertheless, the number of atoms per cubic centimetre will still amount to thousands, even at great distances from the sun.

At the same time, one of the results of the high vacuum will be that the atoms, in consequence of the large free paths, will receive very considerable velocities in the radial direction by virtue of the preponderance of the pressure of the light, just as in the case of the ions of a rarefied gas under the action of an electric field. This velocity will diminish slowly with increasing distance from the sun, for although the propelling force falls off rapidly, the free paths increase at the same time as the rarefaction of the dispersed gas becomes greater. At present we can only say that the magnitude of the velocity might be very large. If it be so large that the atomic ions become positive atomic rays, so that we should have to identify them with the positive rays assumed by Vegard on the basis of the phenomena of the aurora, then of course the kinetic ideas here developed would have to be correspondingly modified, for in such a case the action on the gas of the comet would no longer be that of a simple impact.

It should be pointed out that the absence of the fluorescent light of the coronal gas, which on this view fills planetary space, could be explained by the enormous attenuation and by the diminution of the excitation, which is inversely proportional to the square of the distance from the sun. At the same time it is also possible that the almost continuous band spectrum of the coronal gas is not separable from diffuse daylight or diffuse stellar light owing to its feeble intensity, and that the spectrum of the zodiacal light which is at present simply described as being continuous may yet prove to be in part a band spectrum like that of the outer corona. It has often been maintained that there are relations between the corona and the zodiacal light.

When the comet enters this gas, which is streaming away from the sun with large velocity, the gases developed from its nucleus gravitate of themselves towards the sun, since they will not be excited to resonance, or at least not sufficiently. According to the experiments of Lebedew, the radiation pressure of sunlight on the molecules of acetylene is a thousand times smaller than the gravitational action of the sun. We must assume that, apart from the nucleus, the

density of the comet gases is exceedingly small, but that their temperature is not inconsiderable, even when we are not inclined to interpret their luminosity as of purely thermal origin. The gases of the comet then diffuse with almost molecular velocity into the upward stream of gas driven from the sun by radiation pressure, and the whole process will take place essentially according to the same laws, although at extremely small partial pressures, as were obtained above in the case of the sodium vapour developed from the glass bead. We have first the development of a spherical envelope at great distance from the sun, then a lagging behind of the envelope with respect to the nucleus as the distance from the sun diminishes, and finally the development of a parabolic envelope with the nucleus at its focus, in which case the diameter of the figure above the nucleus becomes smaller. These phases roughly represent the stages in the development of every large comet, and correspond exactly with what we should expect if the stream-velocity and the density of the gas increases, into which the vapours developed from the nucleus diffuse. The presence of a gas spectrum in the tail of the comet is then quite natural.

But, in addition, all the other essential features of the phenomenon of comets can be readily interpreted. This applies to the angles included between the tail and the prolonged radius vector in the plane of the orbit, and to its curvature from the proper-motion of the nucleus. Small angles which can also be included between the tail and the orbital plane are capable of interpretation from the fact that the emission of gas by the sun will be different according to direction and time, and the flow of gas can also obtain small lateral components in virtue of the equalisation of density which takes place in planetary space. The forces of repulsion often ascribed to the nucleus, and the repeatedly observed phenomenon of concentric envelopes one within the other, are explicable from the gradient of partial pressure and the different value of this gradient for the individual gases which are developed from the nucleus. The sharp boundary of the advancing edge of the tail and the diffuse boundary of the edges of the tail behind the nucleus can be explained by the much higher density gradient in the former place. Moreover, we can explain the three types of comet's tails proposed by Bredichin that can be occasionally observed even simultaneously on one comet, on the bases of the different velocity of the molecules and of diffusion of the gases

developed from the nucleus. Here, however, in contradistinction to Bredichin's view, we should have to assign Type I. (long and narrow tails) to the heavier gases and Type II. (short and broad tails) to the light gases, whereas Type III. (feeble tails occurring only in the neighbourhood of perihelion and directed towards the sun) would, in accordance with the general view, have to be interpreted as a dust-cloud formed by the very violent removal of the gas of the nucleus and consisting of coarser solid particles which fall towards the sun. The presence of this dust corresponding to vigorous activity of the nucleus has been established by the detection of reflected sunlight in the heads of comets near the sun. Doubtless the particles constituting this dust will possess all possible magnitudes, and it must be admitted that particles of suitable magnitude, for which light-pressure exceeds gravitation, can also enter into the tails of Types I. and II., which are directed away from the sun. But since here the luminous matter exists mainly in the state of gas, these particles will not decisively determine the form of these tails.

Should these conceptions appear too purely mechanical, and, in particular, if the luminosity of comets should later be recognized as a purely electrical phenomenon, the view developed here would have to be modified, in the sense that the atomic ions which leave the sun are accelerated by light-pressure until they attain the velocity of atomic rays. These rays then excite luminosity in the molecules of the gaseous envelope of the comet through which they pass, and impart to them in addition a certain velocity in the direction of flight, which is distributed over the whole gas of the comet and causes it to stream. Some time ago Vegard * endeavoured to explain the development and the gas nature of comets' tails in this manner, on the assumption of radio-active processes in the sun, however, as the source of the atomic rays.

According to both views, it is not light-pressure, at least not directly, which acts on the gases of the comet, but the action takes place through the agency of matter which is transmitted with large velocity away from the sun.

* *Ann. d. Phys.* xli. p. 641 (1913).

# LXVIII. *Table of Values of the Integral* $\int_0^x K_0(t)dt$.

*By* S. P. Owen, *Royal Grammar School, Newcastle-on-Tyne* *.

THE following tables were constructed for the purpose of an investigation in which occurred the integral

$$\int_0^x K_0(t)dt,$$

the function $K_0(t)$ being the modified Bessel function of the second kind of order zero.

Since no tables of this integral, nor of the modified Struve function, have been computed previously, it may be of interest to set such tables on record.

The integral $\int_0^x K_0(t)dt$ is expressible in the form †

$$\tfrac{1}{2}\pi x\{L_0(x)K_1(x)+L_0'(x)K_0(x)\},$$

where ‡

$$L_0=\sum_{m=0}^{\infty}\frac{(\frac{1}{2}x)^{2m+1}}{\{\Gamma(m+\frac{3}{2})\}^2},$$

$L_0'(x)$ is the derivate of $L_0(x)$, and $K_1(x)$ is Macdonald's form of the modified Bessel function of order unity.

From these results the tables were computed with the help of seven-figure logarithm tables, and so they may be taken as accurate to five significant figures.

When $x$ is large $L_0(x) \backsim I_0(x)$, where $I_0(x)$ is the modified Bessel function of the first kind, while

$$\lim_{x\to\infty}\int_0^x K_0(t)dt=\frac{\pi}{2}.$$

The last formula is a special case of results quoted by Watson (*loc. cit.* p. 388).

| $x$. | $L_0(x)$. | $L_0'(x)$. | $\int_0^x K_0(t)dt$. |
|---|---|---|---|
| 0·02 | 0·01273296 | 0·6367046 | 0·1005627 |
| 0·1 | 0·0637327 | 0·638743 | 0·3421645 |
| 0·5 | 0·3272407 | 0·690562 | 0·9271025 |
| 1 | 0·710243 | 0·863384 | 1·242509 |
| 2 | 1·937433 | 1·739380 | 1·473676 |
| 3 | 4·64741 | 4·033232 | 1·539706 |
| 4 | 11·13105 | 9·79822 | 1·560113 |
| 5 | 27·10592 | 24·36484 | 1·567387 |
| 6 | 67·1245 | 62·2126 | 1·569635 |
| 7 | 168·5005 | 156·0532 | 1·570402 |
| 8 | 427·4832 | 399·884 | 1·570658 |
| 9 | 1093·516 | 1030·92 | 1·570747 |
| 10 | 2815·652 | 2670·995 | 1·570779 |
| 11 | 7288·43 | 6948·87 | 1·570790 |
| 12 | 18948·84 | 18141·25 | 1·570794 |

* Communicated by Prof. G. N. Watson, F.R.S.

† *Cf.* Watson, 'Theory of Bessel Functions,' 1922, p. 752.

‡ *Ibid.* p. 329.

LXIX. *Electrical Properties of Helium.* *By* J. S. Townsend, *M.A., Wykeham Professor of Physics, Oxford, and* S. P. McCallum, *B.A., Rhodes Scholar, Hertford College, Oxford* *.

THE experiments on the photoelectric currents in helium between parallel plate electrodes, arranged in a manner to determine the rate of increase of the current with the distance between the plates, have shown that the electrons set free from the negative electrode by ultra-violet light acquire sufficient energy to ionize molecules by collision before any other process of ionization takes place to an extent which is appreciable in comparison with the effect of ionization by single collisions.

The principal evidence in support of this conclusion consists in the fact that for a certain range of distance between the plates, when the electric force X and gas-pressure $p$ are constant, the currents are in accurate agreement with the formula $n=n_0\epsilon^{\alpha x}$, and the values of $\alpha$ as found experimentally are given in terms of X and $p$ by an equation of the form $\alpha/p=f(X/p)$.

Some interesting results with regard to the energy required to ionize a molecule, and the loss of energy of electrons in collisions with molecules which are not ionized, may be deduced from these experiments by simple calculations which do not involve the mean free paths of the electrons.

These results, however, are not in agreement with the properties of atomic models as indicated by the quantum theory which are considered by some physicists to be satisfactorily established by experiments arranged on the principle of Lenard's method of determining ionizing potentials where the electrons pass through two or more spaces between grids at various potentials. The experiments of this type have been interpreted as showing that there is a series of critical potentials $V_1$, $V_2$, &c. called resonance potentials, which represent the loss of energy of electrons when they collide with molecules with velocities exceeding the velocity corresponding to one of the resonance potentials. The resonance potentials correspond to wave-lengths in the ultra-violet spectrum, and when the radiation from the molecules falls on an electrode, electrons are set free.

The resonance potentials are less than the ionizing

* Communicated by the Authors.

potential $V_0$, so that in cases where electrons are set free from a metal surface with a small velocity and make several collisions with molecules when they move under an electric force through a gas, they would lose their energy in producing resonance effects before attaining the energy corresponding to the ionizing potential. Under these circumstances no appreciable number of molecules would be ionized by collisions. If this be a correct representation of the effects produced by collisions, it would be necessary to assume that the increases in the current obtained by increasing the distance between the electrodes in the parallel plate experiments are due principally to electrons set free from the negative electrode by radiation from the molecules of the gas. A formula for the rate of increase of the current with the distance between the plates which would arise from this process is easily obtained, and it gives values for the currents which differ by such large factors from those observed experimentally, that it is impossible to reconcile the radiation theory with the parallel plate experiments.

Since widely different views are taken as to the effects produced by the collisions of electrons with molecules, it was considered desirable to investigate the conductivity of gases by another method, in order to decide by direct experiment whether there are any additional electrons set free from the negative electrode by radiation from molecules of the gas, using potentials and gas-pressures as in the parallel plate experiments where the current increases with distances between the plates in accordance with the formula $n = n_0 \epsilon^{\alpha x}$.

2. In order to show the ranges of forces and pressures to be adopted in this investigation, it is necessary to give the results of some experiments with the simple form of parallel plate apparatus which has hitherto been generally used. The electrodes were silver plates 6 cm. in diameter, and the conductivity was obtained by the action of ultra-violet light from an external spark-gap, which set free electrons from the negative electrode. The precautions taken to eliminate impurities were the same as those described in the accounts of other experiments with helium which were made in the laboratory.

The results of the experiments with helium at four different pressures (19, 10, 6, and 4 millimetres) are given in Table I. In the experiments at each pressure the distance between the plates was increased in steps of one millimetre from 5 to 10 millimetres, and the currents for the six different distances were measured, using the same electric force of 120 volts per centimetre. The first two lines of figures in

the table give the distances $x$ between the plates in centimetres and the potential V between the plates in volts. The currents $i$ obtained experimentally are given in arbitrary units, taking 100 as the value of the current with the plates at 5 millimetres apart. The values of $\alpha$ were deduced from the ratios of the currents at the shorter distances, and the quantities $n_0\epsilon^{\alpha x}$ are given immediately below the corresponding currents, the constant $n_0\epsilon^{\alpha\times\cdot5}$ being taken as 100.

TABLE I.

| $x$..... | ·5 | ·6 | ·7 | ·8 | ·9 | ·10 |
|---|---|---|---|---|---|---|
| V..... | 60 | 72 | 84 | 96 | 108 | 120 |
| $p$=19 mm. | | | | | | |
| $i$..... | 100 | 136 | 187 | 250 | 337 | 455 |
| $\alpha$=3·05 | | | | | | |
| $n_0\epsilon^{\alpha x}$ ..... | 100 | 137 | 184 | 250 | 338 | 460 |
| $p$=10 mm. | | | | | | |
| $i$..... | 100 | 138 | 198 | 275 | 405 | 615 |
| $\alpha$=3·46 | | | | | | |
| $n_0\epsilon^{\alpha x}$ ..... | 100 | 142 | 200 | 283 | 400 | 566 |
| $p$=6 mm. | | | | | | |
| $i$..... | 100 | 142 | 202 | 292 | 440 | 675 |
| $\alpha$=3·57 | | | | | | |
| $n_0\epsilon^{\alpha x}$ ..... | 100 | 143 | 204 | 292 | 416 | 596 |
| $p$=4 mm. | | | | | | |
| $i$..... | 100 | 140 | 196 | 276 | 426 | 700 |
| $\alpha$=3·37 | | | | | | |
| $n_0\epsilon^{\alpha x}$ ..... | 100 | 140 | 196 | 275 | 385 | 540 |

Allowing for an experimental error of about 2 per cent., it is seen that the currents are in agreement with the formula within certain ranges of potential. With the pressure 19 millimetres, the ratio $X/p$ being 6·31, the agreement extends up to a potential of 120 volts. The range diminishes with the pressure, as shown by the figures in the last column where the values of $i$ are much greater than the quantities $n_0\epsilon^{\alpha x}$ with the pressures 10, 6, 4 millimetres. At the lowest pressure, 4 millimetres, where the ratio $X/p$ is 30, the limit of the range of potential where the currents are in agreement with the formula is between 96 and 108 volts, but there is no abrupt change to indicate the exact limit of the range.

3. These experiments have been interpreted as showing that the increase of the conductivity of the gas with the distance between the plates is due to ionization of molecules of the gas by the collisions of electrons when the currents increase with the distance in accordance with the formula $n_0\epsilon^{\alpha x}$, and that there is no appreciable effect due to any other process of ionization under these circumstances.

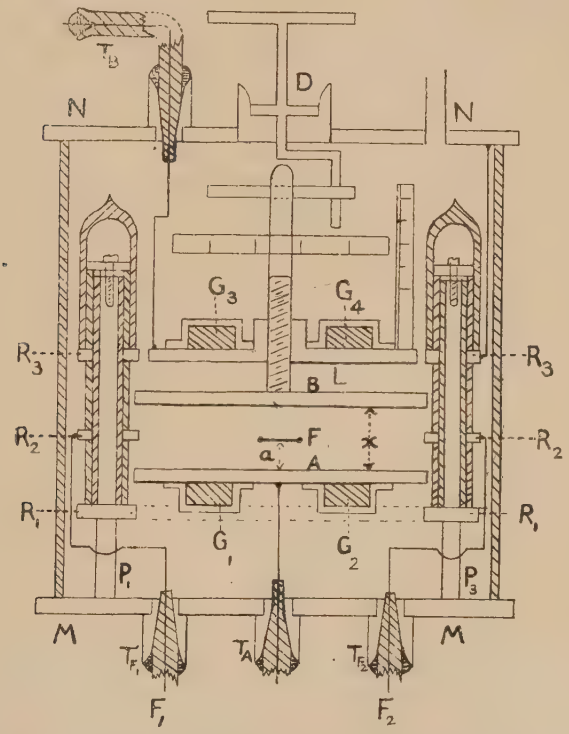
With larger distances between the plates, where the rate of increase of the current with the distance exceeds the rate of increase of the quantity $n_0\epsilon^{\alpha x}$, some additional process of ionization begins to produce an appreciable effect. This effect may be due to ionization of molecules by the collisions of positive ions, or to electrons set free from the negative electrode by the impacts of positive ions, or to electrons set free from the electrode by radiation from molecules of the gas. For the purpose of this investigation it is not necessary to decide which of these processes is the most important. They have some features in common which make it possible to obtain direct experimental evidence in support of this theory by measuring the currents obtained in a modified form of apparatus with two parallel plates.

4. The method of investigation which has been adopted for this purpose, involves the measurement of the currents to the two plate electrodes A and B (shown in fig. 1). The electrodes were 8·8 cm. in diameter and were plated with silver. A short filament F of fine platinum wire was set up between them at a fixed distance ($a$) from the lower plate A. The upper plate B was mounted on an axle with a micrometer screw so that it was possible to adjust the distance $x$ between the two plates to any length from 10 to 18 millimetres. The distance $a$ of the filament from the lower plate was 7 millimetres. The filament was supported by two fine silver wires (as shown in fig. 2), which also lay in the plane at 7 millimetres from the lower plate.

The insulators were of glass, and are shaded in the diagram (fig. 1) to distinguish them from the metal parts which were made of silver-plated brass. The apparatus was enclosed in a glass cylinder, cemented to the metal base M and to the top cover-plate N. The brass ring $R_1$ was fixed to the base by four short brass rods, two of which, $P_1$ and $P_3$, are shown in the diagram. Four longer rods formed continuations of the short rods to carry the rings $R_2$ and $R_3$, from which they were insulated by sleeves of glass tubing. The sleeves fitted the rods and passed through holes in the rings. The rings $R_2$ and $R_3$ were held in position parallel to the ring $R_1$ by

wider glass sleeves ground to exact lengths. The upper parts of the brass rods and the clamping screws were covered with glass tubing to prevent any discharge which might pass from the rods to the upper parts of the apparatus, as in some of the experiments the potential of the upper parts was 130 volts.

Fig. 1.




The plate A rested on two insulating plate-glass strips $G_1$ $G_2$ clamped to the plate and the lower ring $R_1$.

The brass plate L with the micrometer thread was clamped to the two insulating plate-glass strips $G_3$ $G_4$, which were fixed to the upper ring $R_3$.

The ring $R_3$ was connected to the cover plate N, and was maintained by a battery of cells at the potential to which the upper plate B was charged. With this arrangement, when the plate B was insulated the charge did not tend to leak over the surface of the glass insulators.

The micrometer screw carrying the plate B was rotated

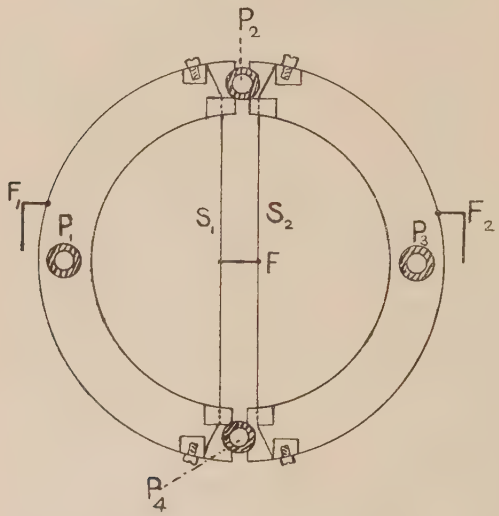
by the axle D resting on a flat bearing in the cover-plate, and the bearing was made air-tight with tap-grease.

The connexion to the plate A was made through a long glass capillary tube $T_A$ ground to fit a tapered brass socket in the base, and was made air-tight by cement on the outside.

The connexion to the plate B was made in a similar manner through the cover-plate N by the capillary tube $T_B$.

The ring $R_2$ was split along the diameter through the rods $P_2$ and $P_4$, as shown in fig. 2. Two silver wires, $S_1$ and

Fig. 2.




$S_2$, were stretched tightly between the ends of the sections at seven millimetres apart, and the platinum filament F was soldered to the silvered wires. The connexions to the sections of the ring were made through the wires $F_1$ and $F_2$ which carried the heating current. These wires passed through insulating glass tubing fitted into sockets in the base, as shown in fig. 1.

5. In each experiment the lower plate A was at zero potential, the filament was maintained at a potential V by a battery of small accumulators, and the upper plate B was charged to the potential $Vx/a$. A uniform electric force X was thus established in the field between the two plates, except in a small space near the filament and the silver wires where the uniformity of the field of force is disturbed

by the surface distribution on the wires. There is no appreciable change in the distribution of the electric force near the filament when the distance $x$ is changed from $x_1$ to $x_2$ and the potential of the upper plate changed from $Vx_1/a$ to $Vx_2/a$. The latter potentials were carefully adjusted with a potentiometer, as it was found that there was a large change in the number of electrons passing from the filament to the lower plate A due to a small change in the potential of B. The investigation of the properties of the conductivity considered in section 3 depends on measurements of the ratio of the currents to the plates A and B, and is not affected by small errors in the adjustment of the potential of the plate B. It is, however, of advantage to adjust these potentials accurately, in order to represent the currents by continuous curves in terms of the potential V.

The filament was heated to a dull red by a battery of large accumulators, and the current was maintained for a considerable time until the electron emission became constant. The fall of potential between the terminals leading to the filament was about a quarter of a volt, so that no appreciable error is introduced in taking the potential of the filament and the wires supporting it as being at the potential V of the centre of the filament.

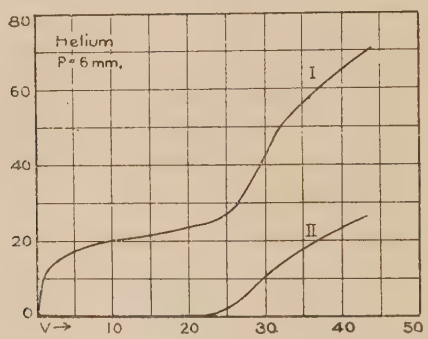
The currents to the plates were found by a zero method with an induction balance, so that when the plates were insulated their potentials did not change by more than a small fraction of a volt while the currents which they received through the gas were being measured. A sensitive quadrant-electrometer was used as the indicator in connexion with the balance, and small emission currents from the filament were used in order to avoid any disturbance of the field by the charges of the electrons or positive ions in the space between the plates. The relative values of the currents obtained with different forces were, in all cases, independent of the intensity of the filament emission.

6. When the potentials V and $Vx/a$ of the filament and the upper plate are negative, a stream of electrons flows to the lower plate and, with large potentials, the upper plate receives a positive current. The currents flowing to the two plates were measured with a constant filament emission and a constant distance of 12 millimetres between the plates for different fields of force obtained by altering the potentials of the filament and upper plate, the potential of the latter being adjusted to 12 V/7 when the filament was at the potential V.

The currents obtained with helium at a pressure of

6 mm. are represented by the curves (fig. 3) in terms of the potential V of the filament, the ordinates of Curve I. being the negative currents through the gas to the lower plate, and the ordinates of Curve II. the positive currents to the upper plate. The currents were obtained in the ordinary manner by making a series of observations of the quantities of electricity received by the plates in equal intervals of time. The induction balance was adapted to measure the charges received by the two plates during the same interval of time. The ratio of the two currents was thus obtained very accurately, since by this method there is no error due to fluctuations in the filament emission. The ratios thus found were in good agreement with the ratios of the ordinates of the two current electromotive force curves given in fig. 3.

Fig. 3.




Curve I. shows that there is a small increase in the negative current to the lower plate as the potential V is increased from 10 to 20 volts, due to additional electrons from the filament, and a large increase due principally to some process of ionization in the gas with the larger forces from 20 to 40 volts. Curve II. leads to the same conclusion, as the positive current to the upper plate is very small (due to a small positive emission from the filament), while V is less than 20 volts, but increases rapidly with the larger values of V.

7. The point to be decided is whether the increases in the currents obtained when V is increased from 20 to 40 volts can be attributed to any cause except the direct ionization by the collisions of electrons with molecules in the space between the filament and the lower plate. For example, let it be supposed that the electrons emitted from the filament excite radiation in colliding with molecules in the space

between the filament and the lower plate, and that this radiation sets free electrons from the upper plate. Let $n_1$ be the number of electrons emitted from the filament $n_2$ the corresponding number set free from the upper plate by the radiation excited by the electrons from the filament. The electrons thus set free from the upper plate also collide with molecules, and by a similar process the number $n_2$ becomes multiplied to $rn_2$, and the total effect corresponding to any value of V from 20 to 40 volts is represented by the ordinate of Curve II. (fig. 3). The action is now exactly similar to that observed in the simple case of parallel-plate electrodes when ultra-violet light from an external spark-gap falls on the negative electrode, and the experiments recorded in Table I. show that large increases in the factor $r$ may be obtained when the electric force and gas-pressure are constant and the distance between the plates is increased.

If the distance between the plates be increased from 12 to 17·5 millimetres and the potential of the upper plate increased from 12 V/7 to 17·5 V/7 when the filament is at the potential V, the curves, fig. 3, would assume a different form. While the ordinates from V = 10 to V = 20 remain constant, the ordinates of both curves from V = 20 to V = 40 would be increased. The change to be expected may be found by considering the ordinate of Curve II. at the point corresponding to V = 40. At this point the potential of the upper plate is 68·5 volts when $x = 12$ mm. and 100 volts when $x = 17{\cdot}5$ mm., thus the increase in distance involves an increase of 31·5 volts in the potential difference between the plates. The ordinate of Curve II. would therefore be increased by a factor of 2 at least, since the experiments recorded in Table I. show that the current is increased from $i$ to $2i$ approximately when the distance between the plates is increased by an amount involving an increase of 24 volts in the potential difference between the plates. Thus the radiation hypothesis leads to a conclusion which differs widely from that indicated by the theory of ionization by collision.

According to the latter theory, the increases in the current with the potential V are due to the ionization of molecules in the space between the filament and the lower plate, and the rate of increase of the current with the potential would not be affected by increasing the distance between the plates, provided the total potential difference between the plates does not exceed 100 volts and the pressure of the gas is above 3 millimetres. This limit of pressure is indicated by the third experiment in Table I., where $X/p = 20$, if the

effect of the increase of temperature of the gas due to the filament be neglected.

8. Experiments were therefore made with the apparatus shown in fig. 1, the distance between the plates being 17·5 mm. instead of 12 mm., and it was found that with the gas at 6 mm. pressure the two curves representing the currents to the lower and upper plates with $x=17{\cdot}5$ mm. were precisely the same as those given in fig. 3 for the distance $x=12$.

The experiments were repeated several times with gas that had been used in the apparatus for some days and with a fresh supply of gas that had been kept for a few hours in a charcoal tube cooled with liquid air, and no change was observed in the rate of increase of the current to either plate with the potential V when the distance between the plates was changed from 12 to 17·5 millimetres, the maximum potential difference between the plates being 100 volts. These experiments were made with pressures of the gas from 4 to 20 mm.

Under these conditions, therefore, it must be concluded that there is no effect due to electrons set free from the negative electrode by radiation from molecules of the gas which is comparable with the effect of direct ionization by the collisions of electrons with molecules of the gas.

It is also easily seen that the positive ions make no appreciable contribution to the conductivity in these experiments either by ionizing molecules of gas or by setting free electrons from the negative electrode, for in these processes of ionization the action would be increased by increasing the distance between the electrodes as in the case of radiation.

9. The collision theory explained in section 3 receives further support when larger potential differences are used between the plates A and B (fig. 1). In the experiments with the photoelectric currents recorded in Table I. where the rate of increase of the current with the distance $x$ exceeds the rate of increase of the quantity $n_0\epsilon^{ax}$, the change in the mode of development of the current has been attributed to one of three processes. In the second experiment (Table I.), where the gas was at 10 millimetres pressure, the distance between the plates one centimetre, and the potential $V=120$ volts, the effect of the additional process of ionization is shown by the divergence between the figures 615 and 566.

In experiments of this type it has been found that the divergence from the formula obtained with a given potential difference V depends only on the ratio $X/p$. Thus if the

force were 60 volts per centimetre and the pressure 5 millimetres, the current with a distance of 2 centimetres between the plates would exceed the corresponding quantity $n_0\epsilon^{\alpha x}$ by the same factor 615 : 566.

The experiments given in the table may therefore be taken as showing that with a potential difference between the plates of 96 volts there is no additional process of ionization at any pressure for which the ratio $X/p$ is less than 30. With 120 volts there is a distinct effect when $X/p=12$, which becomes more marked as the ratio $X/p$ increases. When $X/p=30$ a distinct additional effect is obtained with the potential 108 volts, as shown by the experiments with the gas at 4 millimetres pressure.

In experiments with the arrangement of electrodes shown in fig. 1 where the filament is 7 millimetres from the lower plate, the electric force is 68·5 volts per centimetre when the potential of the filament is 48 volts, the upper plate being at 82 volts when $x=12$ and at 120 volts when $x=17{\cdot}5$. The above theory therefore shows that with $x=12$ millimetres and the gas-pressure above 2·3 millimetres, the increases in the currents to the electrodes obtained by increasing the potential of the filament from 10 to 48 volts are due to ionization by collision of electrons with molecules of the gas, no other process of ionization having an appreciable effect. With $x=17{\cdot}5$ millimetres an additional process of ionization should be appreciable with the larger forces, and the effect should become more marked as the pressure is reduced.

10. The results of the experiments with the larger forces are shown by the curves (figs. 4 & 5). With the gas at 10 millimetres pressure and the plates 12 millimetres apart, the currents to the lower and upper plates (A and B, fig. 1) are given by the curves $i_1$ and $i_2$ (fig. 4). With the gas at the same pressure and the plates 17·5 millimetres apart the currents are given by the curves $i'_1$ and $i'_2$. The curve $i_1$ coincides with the curve $i'_1$ and $i_2$ with $i'_2$ for potentials of the filament less than 48 volts. With the filament at 55 volts the currents corresponding to $x=17{\cdot}5$ are greater than those for $x=12$. In these experiments ($p=10$ mm.) when $V=48$ volts, the value of $X/p$ is 6·85 and the potential difference between the plates is 120 volts with $x=17{\cdot}5$. The absence of any additional process of ionization up to this point is in agreement with the theory of the photoelectric currents recorded in the first experiment (Table I.), where $X=120$ volts per centimetre and $p=19$ millimetres, $X/p$ being 6·3.

Fig. 4.

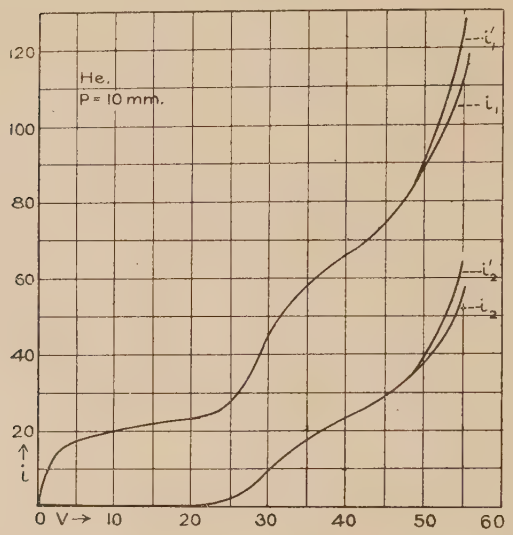
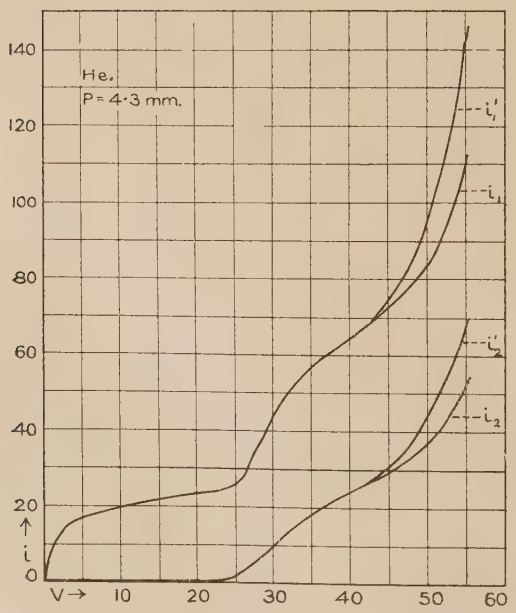

He.
P = 10 mm.
120
100
80
60
40
20
i
0 V→ 10 20 30 40 50 60
--- i'1
--- i1
--- i'2
--- i2

Fig. 5.


He.
P = 4·3 mm.
140
120
100
80
60
40
20
i
0
V→ 10 20 30 40 50 60
--- i'1
--- i1
--- i'2
--- i2

The figures in Table I. indicate that all additional processes of ionization are absent up to a higher point with smaller values of the ratio $X/p$. This was found to be the case with the filament currents through the gas at 20 millimetres pressure. The currents to the lower and upper plates for all potentials V of the filament up to 55 volts were the same for the two distances between the plates $x=12$ and $x=17{\cdot}5$ millimetres, the potential difference between the plates being 137 volts when $x = 17{\cdot}5$ millimetres and V = 55 volts.

With pressures less than 10 millimetres the curves representing the currents to the two plates for the two distances $x=12$ millimetres and $x=17{\cdot}5$ millimetres are more divergent, and the divergence occurs with smaller values of V than is indicated by the curves (fig. 4).

With the gas at 6 mm. pressure there was a distinct increase in the currents to both plates with the filament at 48 volts, due to changing $x$ from 12 to 17·5 millimetres.

With the gas at 4·3 mm. pressure the increase in the currents to the two plates due to changing $x$ from 12 to 17·5 millimetres was much more marked. The values of $i_1$ and $i_2$ corresponding to $x=12$, and $i'_1$ and $i'_2$ corresponding to $x=17{\cdot}5$, are given by the curves (fig. 5).

The experiments show that the additional process of ionization which causes the divergence between the curves (figs. 4 & 5) rises in importance as the value of $X/p$ increases, in the same way as the values of the current $i$ exceed the quantity $n_0 e^{ax}$ in the experiments with the photo-electric currents recorded in Table I. It would be difficult to obtain evidence of an exact agreement between the two methods of indicating the points at which the additional process of ionization becomes appreciable, as this would involve an estimate of the rise of temperature of the gas due to the heated filament, and of the action of the wires supporting the filament in intercepting electrons and positive ions in the space between the plates.

It is of importance, however, to show that the rate at which molecules are ionized by the collisions of electrons is the same in the photoelectric and thermionic currents, but for this purpose it is better to consider the currents obtained with the heated filament when the electric force is reversed and the stream of electrons from the filament traverses different distances $(x-a)$ through the gas to the upper plate B (fig. 1).

11. The preceding investigation does not indicate the exact cause of the additional ionization, except that it cannot

be attributed to a photoelectric action of radiation from molecules of the gas of the type which has been suggested. If the molecules emit radiation in consequence of the collisions of electrons moving with velocities corresponding to a series of resonance potentials, $V_1$, $V_2$, &c., less than the ionizing potential $V_i$ but of the same order, the photoelectric effect of the radiation should rise and fall with the pressure when the electric force is constant approximately in the same manner as the quantity $\alpha$ varies with pressure in the experiments given in Table I. These experiments show that $\alpha$ diminishes as the pressure is reduced from 6 to 4 millimetres, but the additional process of ionization which causes the currents to exceed the quantity $n_0\epsilon^{\alpha x}$ rises in importance. Since the effect increases continuously with the large values of the ratio $X/p$, it appears to be due to positive ions which become more active as their velocity increases, or to radiation excited by collisions of electrons when moving with velocities much greater than that required to ionize molecules of the gas.

The remarkable feature of this action is that it is so large in the monatomic gases. In helium it is appreciable in currents between parallel plates when the potential difference between the plates is 108 volts and the ratio $X/p$ is 30. In hydrogen when the ratio $X/p$ is 88, the corresponding effect does not become appreciable until the potential difference between the plates is 200 volts.

It is probable that the action is due to positive ions which acquire more energy in helium than in hydrogen under the action of an electric force, as the loss of energy of the ions in collisions with molecules which are not ionized would be less in monatomic than in diatomic gases. The collisions of a positive ion with molecules which are not ionized may be supposed to resemble the collisions of a molecule (A) which had acquired a large energy of translation exceeding the energy of translation of the surrounding molecules. In monatomic gases the molecule (A) loses energy in collisions owing to the transfer of momentum, but in diatomic gases energy is lost both by the transfer of momentum and the conversion of energy of translation into energy of rotation.

12. In the papers describing the results of previous experiments with helium, it has been shown that the large effects due to ionization by the collisions of electrons with molecules cannot be explained on the hypothesis that a molecule is "partially ionized" by one collision and complete ionization is obtained by a second collision. Also, with the photoelectric currents, the fact that the activity of

the electrons is independent of the intensity of the ultra-violet light from the external spark-gap indicates that this light does not affect the molecules of the gas.

It has however been suggested that even with light of small intensity the molecules may become "partially ionized," and the large effects obtained by single impacts of electrons with molecules may be due to this cause.

In view of this objection, it was considered desirable to find the activity of the electrons from measurements of the conductivity obtained by means of a heated filament, and to compare the result with the activity found in the experiments where electrons are set free from the negative electrode by ultra-violet light from an external spark-gap. The small currents suitable for this purpose are obtained when the filament is heated to a dull red so that there are no rays from the filament which can affect the molecules of the gas.

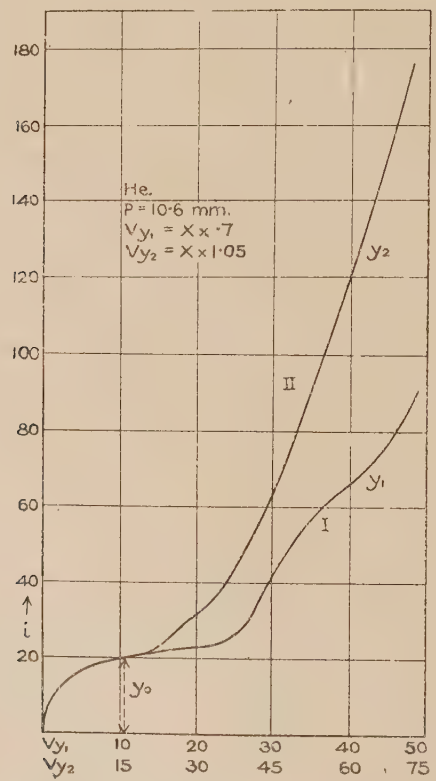
It is difficult to find the rate at which molecules are ionized from a curve representing the current in terms of the potential difference between the electrodes such as Curve I. (fig. 3), since the increase of the current with the potential is due partly to additional electrons coming from the filament. This difficulty is avoided by reversing the electric force and measuring the currents of electrons to the upper plate B (fig. 1) when it is set at two different distances $(x_1-a)$ and $(x_2-a)$ from the filament. The temperature of the filament is affected by varying the distance between the plates so that it is necessary to measure the currents $y_1$ corresponding to different forces X with the upper plate at a fixed distance $(x_1-a)$ from the filament, and after changing the distance to $(x_2-a)$ and adjusting the temperature of the filament, to measure the currents $y_2$ corresponding to the same electric forces. The currents $y_1$ with the plate B at 7 mm. from the filament are given by Curve I. (fig. 6); the currents $y_2$ with the plate B 10·5 mm. from the filament are given by Curve II., the electric force X being in volts per centimetre, and the gas-pressure 10·6 mm.

The same ordinate $y_0=20$ is taken to represent the current with the lowest force in each curve. The difference between the ordinates $(y_2-y_1)$ corresponding to a large force X represents the number of molecules ionized in the space between the two planes $x_1$ and $x_2$, and $y_1$ the number entering the space. Since the currents $y_1$ and $y_2$ are obtained with the same electric force X, the number of electrons coming from the filament is the same in each case.

In moving under a uniform electric force through a gas

the electrons do not attain a steady motion until they have traversed a certain distance from the filament. Experiments with photoelectric currents in helium show that the energy of the electrons increases up to a point where about half the electrons from the negative electrode have ionized molecules of the gas. After passing this point there is a slight decrease in the average energy of the electrons in the

Fig. 6.




stream, and the motion approaches a steady state after the stream has traversed a distance $b$ from the electrode where $Xb$ is about 45 or 50 volts when the ratio $X/p$ is about 16 and the gas at 16° C. For distances from the negative electrodes greater than $b$ the currents increase with the distance in accordance with the formula $n_0\epsilon^{\alpha x}$.

In order to estimate the rate at which electrons ionize molecules, when the motion is steady, from the ratio of the

ordinates of the two curves (fig. 6) it is necessary that the potential difference between the filament and the plate B should exceed 45 volts. In order that this condition may be satisfied when the plate is 7 mm. from the filament the value of X should exceed 64 volts per centimetre.

There is also an upper limit to the value of X depending on the potential difference $X \times x$ between the two plates A and B (fig. 1). The curves (fig. 3) show that when the gas is at 10 mm. pressure, the additional process of ionization contributes to the conductivity, when the potential difference $X \times 1{\cdot}75$ exceeds 125 volts. In order to avoid this effect when the electrons are moving to the upper plate and the distance between the plates is 17·5 millimetres, the electric force should not exceed 70 volts per centimetre.

Hence in the curves (fig. 6), when the the electric force is between 64 and 70 volts per centimetre, the difference $(y_2 - y_1)$ of the ordinates corresponding to the same value of X represents the number of molecules ionized by electrons moving through the distance $(x_2 - x_1)$ equal to 3·5 millimetres, when the motion of the electrons is steady. At the points on the curves corresponding to X = 67 ($V_{y1} = 47$ volts) the ratio of the ordinates $y_2/y_1 = 2{\cdot}0$, which shows that the number of electrons in the stream is exactly doubled in moving through the distance $(x_2 - x_1)$, where $(x_2 - x_1)X = {\cdot}35 \times 67 = 23{\cdot}4$ volts.

The gas in these experiments was at 10·6 millimetres pressure, but the average temperature was at least twice the normal in the space traversed by the stream of electrons from the filament to the upper plate. The value of $X/p$ must therefore be taken to be about 14 in these experiments in order to compare the results with those obtained in a gas at 16° C.

The photoelectric currents obtained in helium at about 16° C. (given in Table I.) show that the quantity $\alpha$ does not change to any great extent when $X/p$ varies from 12 to 20, and at these points the photoelectric current is doubled in moving through the distance $(x_2 - x_1)$, where $(x_2 - x_1)$ X is about 23 or 24 volts.

It is evident, therefore, that the action of electrons in ionizing molecules of helium when the gas is traversed by ultra-violet light does not differ appreciably from the action in the absence of ultra-violet light.

LXX. *Some Dynamical Illustrations of the Pressure of Radiation and of Adiabatic Invariance.* *By* T. H. Havelock, *F.R.S.**

*Introduction.*

1. THE associated ideas of the pressure of vibrations and of certain adiabatic invariants suggest various problems in simple dynamical systems with a moving constraint which are capable of exact solution.

The first one considered is the small transverse vibration of a particle attached to a light string whose tension is assumed constant. One end of the string is fixed; while on the other side of the particle the string passes through a small hole in a plate which is made to move with uniform velocity $v$. The differential equation of motion can be solved completely in terms of generalized hypergeometric functions; here we require a solution for which the initial position and velocity of the particle have assigned values, and it is more convenient to work out directly an asymptotic expansion for such a solution as $v$ converges to zero. If the plate is moved through any finite distance, we may then calculate the final motion in terms of the initial motion to any required degree of accuracy; in particular, if E is the energy of the motion and $n$ the corresponding frequency, we may examine how the final value of $E/n$ approximates to its initial value when $v$ is made small.

A special case of this problem is obtained by taking the constant length of string on one side of the particle to be infinite, or supposing the particle to move in smooth guides at right angles to the string. Here the complete solution involves more familiar Bessel functions, of which asymptotic expansions are available. This case is essentially the same as the so-called Rayleigh pendulum, and I find that a similar solution of the latter problem has been given recently by Krutkow and Fock †.

Further interest attaches to the similar problems when the vibrating medium is a continuous uniform string. These include the well-known device by which Larmor illustrated the pressure of radiation. By considering incident and reflected simple harmonic waves at a moving reflector, he obtained the pressure of radiation in the form

$$p = \frac{c^2 - v^2}{c^2 + v^2} e_R, \quad \ldots \ldots \quad (1)$$

* Communicated by the Author.

† G. Krutkow and V. Fock, *Zeit. für Phys.* xiii. p. 195 (1923).

where $c$ is the wave velocity, $v$ the velocity of the reflector, and $e_R$ the density of energy in front of the reflector; it should be noted that $p$ and $e$ have in his analysis their average values for simple harmonic waves.

Levi-Civita * refers to the case when the string is of finite length, one end being fixed and the other passing through a moving plate; he remarks that it would not be difficult to determine functions satisfying rigorously the nodal condition both at the fixed end and at the moving reflector. The solution is supplied in the following paper; it was, in fact, this remark which suggested the problems considered here. The solutions examined are those which reduce to simple harmonic vibrations when the velocity of the moving reflector is made infinitesimal; they are used to calculate the pressure on the reflector and also to confirm the adiabatic invariance of $E/n$ in these cases.

Larmor's formula (1) is usually referred to as being valid for a non-dispersive medium in which the average density of energy in a simple harmonic wave is inversely proportional to the square of the wave-length. From this point of view it could be extended to other types of disturbance in such a medium by direct summation †. However, if we remove the restriction that we are dealing with average values of the pressure and of the energy density, it is easy to generalize the result completely from the equations of motion together with the kinematic condition for a travelling node. This is confirmed also by the properties of the general solution when there is a stationary node and a travelling node.

The same arguments apply equally to electromagnetic waves in free space when suitable conditions are chosen for the travelling node.

It is desirable to specify clearly what is meant by the pressure of radiation. Calculations are generally made on the assumption of simple harmonic vibrations and average values are used, the pressure being usually deduced by an application of Lagrange's dynamical equations in generalized coordinates. Here we consider in each case an unlimited medium in which there is a disturbance, which can be analysed into forward and backward waves, such that there is a fixed node and a node travelling away from it with uniform velocity $v$; the pressure is defined as the rate of decrease of energy in the region between the two nodes divided by the velocity $v$.

* T. Levi-Civita, Appendix to Sir Joseph Larmor's lecture on "The Dynamics of Radiation," Inter. Math. Congress, Proc. i. p. 217 (1912).

† Ghosh and Sur, Phys. Rev. xviii. p. 380 (1921).

The actual apparatus for a moving reflector by which this pressure could be realized is of course quite another matter. For a string, a plate with a hole through which the string passes is sufficiently descriptive; but it is no more than that—in fact, the resolved force on the plate due to the tension of the string is not in general equal to the pressure as calculated. One may refer here to some rather artificial devices suggested by Poynting * by which one might imagine this pressure realized in certain cases, such as the motion of a plate through a gas or an elastic solid; incidentally, Poynting refers to the pitfalls which beset the subject, the two chief being the definition of the pressure and the fact that when second-order terms are used for its calculation the original equations may no longer be valid and it may not be permissible to assume simple harmonic motion. In a recent elaborate study by Brillouin † the distinction is carefully drawn between the pressure on an ideal reflector immersed in a continuous medium and the pressure on a reflector which bounds the medium; the conclusion seems to be drawn that most previous writers, with the exception of Lorentz, have failed to observe the distinction.

However, we are not concerned specially with these considerations in what follows; the problems are comparatively simple dynamical cases in which the conditions are specified in the manner indicated, and assuming these conditions certain exact solutions of the equations of motion are investigated.

In a last section some application is made to dispersive media, the example being a uniform string at constant tension in which each particle is attracted to its equilibrium position by a force proportional to displacement. From considerations of energy changes, it appears that the formula (1) for the pressure of radiation holds also in this case, when suitably interpreted. This is also confirmed for the particular case of simple harmonic waves incident upon and reflected by a moving reflector; further, when average values are considered, the connexion with group velocity and flow of energy is shown.

For a fixed reflector it follows that the pressure is equal to the density of energy in front of the reflector. This is in apparent contradiction with the usual statement for a dispersive medium, that the pressure is U/V times the energy density, where V is wave velocity and U is group velocity. The results are harmonized by noticing that in the latter

* J. H. Poynting, Phil. Mag. ix. p. 393 (1905).

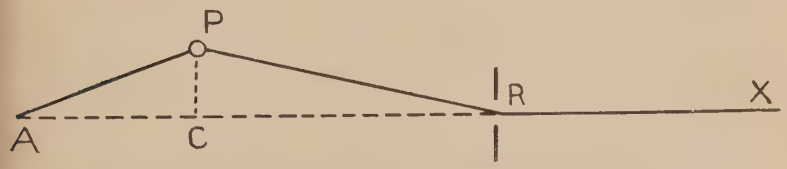
† L. Brillouin, "La Theorie de Solides et les Quanta," *Ann. Ecol. Norm.* xxxvii. (1920).

expression the result only applies to simple harmonic waves and the energy density in question is the average value over the whole range of medium in front of the reflector; the result obtained here is more general, and in it the energy density is that immediately in front of the reflector.

*Vibrations of a Particle.*

2. A particle P of mass $m$ is attached to a light string APRX stretched at constant tension T; R is a plate with a small smooth hole through which the string passes.

Fig. 1.




If AC$=a$, and CR$=b+vt$, the equation of motion for small displacement $y$ is, with the usual approximation,

$$(b+vt)\frac{d^2y}{dt^2}+\frac{\mathrm{T}}{ma}(a+b+vt)y=0. \quad . \quad . \quad . \quad (2)$$

If we take the energy at any instant to be

$$\mathrm{E}=\tfrac{1}{2}m\dot{y}^2+\tfrac{1}{2}\mathrm{T}y^2\left(\frac{1}{a}+\frac{1}{b+vt}\right), \quad . \quad . \quad . \quad (3)$$

then from the definition already given, the pressure $p$ of the vibrations upon the plate R is

$$p=-\frac{1}{v}\dot{\mathrm{E}}=\tfrac{1}{2}\mathrm{T}\frac{y^2}{(b+vt)^2}, \quad . \quad . \quad . \quad . \quad (4)$$

after using (2). To this order, the value is the same as the resolved force on the plate, namely T(1$-\cos$ PRC). The same result also follows if we use the Lagrange equations with the length CR as a generalized coordinate. No discrepancy arises in this case, since the moving constraint affects one of the parameters of the system without acting directly upon the coordinates of the particle. We shall see later that it is different when we take into account the inertia of the string.

3. We require the solution of (2) when $y$ and $\dot{y}$ have given initial values and in a form suitable for small values of $v$ but with $vt$ finite.

If we put

$$x = (b+vt)/a\,; \qquad k^2 = a\mathrm{T}/mv^2, \quad . \quad . \quad . \quad (5)$$

the equation becomes

$$\frac{d^2y}{dx^2} + k^2\left(1+\frac{1}{x}\right)y = 0. \quad . \quad . \quad . \quad . \quad (6)$$

The complete solution may be written in various alternative forms; for instance,

$$y = \mathrm{A}W_{-\frac{1}{2}ki,\,\frac{1}{2}}(2ikx) + \mathrm{B}W_{\frac{1}{2}ki,\,\frac{1}{2}}(-2ikx), \quad . \quad . \quad (7)$$

where A, B are arbitrary constants, and $W_{m,\,n}$ is a confluent hypergeometric function. However, it is more direct to obtain from the differential equation (6) an asymptotic expansion of the required solution suitable for large values of the parameter $k$.

We shall use accents to denote differentiation with respect to $x$: then if $y_0$ and $\dot{y}_0$ are the initial values for equation (2), those for equation (6) are

$$y = y_0\,; \quad y' = k\dot{y}_0\sqrt{(am/\mathrm{T})}\,; \quad \text{for } x = b/a = x_0. \quad . \quad (8)$$

Assume a solution of the form

$$y = e^{ik\omega}\left(\phi_0 + \frac{\phi_1}{k} + \frac{\phi_2}{k^2} + \ldots\right), \quad . \quad . \quad . \quad (9)$$

where $\omega$, $\phi_0$, $\phi_1$, ... are functions of $x$. Substitute in (6) and equate to zero the coefficients of $k^2$, $k$, $k^0$, $k^{-1}$, ...; we then obtain the series of equations

$$\left.\begin{aligned} \omega'^2 &= 1+x^{-1}, \\ \omega''\phi_0 + 2\omega'\phi_0' &= 0, \\ i\omega''\phi_1 + 2i\omega'\phi_1' + \phi_0'' &= 0, \\ i\omega''\phi_2 + 2i\omega'\phi_2' + \phi_1'' &= 0, \\ &\ldots\ldots\ldots\ldots \\ &\ldots\ldots\ldots\ldots \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

Similarly, if we assume a solution

$$y = e^{-ik\omega}\left(\psi_0 + \frac{\psi_1}{k} + \frac{\psi_2}{k^2} + \ldots\right), \quad . \quad . \quad . \quad (11)$$

we obtain a set of equations like (10) with $-i$ instead of $+i$. The equations for $\omega$ and the $\phi$'s and $\psi$'s are differential equations of the first order which can be solved for the various functions step by step.

We now take the complete solution to be the sum of (9) and (11), and we have to satisfy the initial conditions (8). For this purpose we take, from the first two equations in (10),

$$\omega = \int_{x_0}^{x} \sqrt{(1+x^{-1})}\,.\,dx, \quad . \quad . \quad . \quad . \quad (12)$$

and then the initial conditions give, for $x = x_0$,

$$\left.\begin{aligned} \phi_0 + \psi_0 &= y_0, \\ i\omega'\phi_0 - i\omega'\psi_0 &= \dot{y}_0\sqrt{(am/\mathrm{T})}, \\ \phi_n + \psi_n &= 0, \\ i\omega'(\phi_n - \psi_n) + \phi'_{n-1} + \psi'_{n-1} &= 0, \end{aligned}\right\} \quad . \quad . \quad (13)$$

for $n = 1, 2, 3, \ldots$.

These give the following values:

$$\left.\begin{aligned} \phi_0(x_0) &= \tfrac{1}{2}y_0 - \tfrac{1}{2}i\dot{y}_0\sqrt{(am/\mathrm{T})}\,/\,\omega'(x_0), \\ \phi_1(x_0) &= \tfrac{1}{4}iy_0\omega''(x_0)\,/\,\{\omega'(x_0)\}^2, \\ \phi_n(x_0) &= 0\,; \quad n = 2, 3, \ldots. \end{aligned}\right\} \quad . \quad . \quad (14)$$

with similar values for the $\psi$'s with the sign of $i$ changed.

We can now integrate completely the subsidiary equations (13), and obtain

$$\phi_0 = \left\{\tfrac{1}{2}y_0 - \tfrac{1}{2}i\frac{\dot{y}_0\sqrt{(am/\mathrm{T})}}{\omega'(x_0)}\right\}\left\{\frac{\omega'(x_0)}{\omega'(x)}\right\}^{\frac{1}{2}},$$

$$\phi_1 = \frac{i}{2\{\omega'(x)\}^{\frac{1}{2}}}\int_{x_0}^{x}\frac{\phi_0''(x)}{\{\omega'(x)\}^{\frac{1}{2}}}dx + \tfrac{1}{4}iy_0\frac{\omega''(x_0)}{\{\omega'(x)\}^{\frac{1}{2}}\{\omega'(x_0)\}^{3/2}},$$

$$\phi_n = \frac{i}{2\{\omega'(x)\}^{\frac{1}{2}}}\int_{x_0}^{x}\frac{\phi''_{n-1}(x)}{\{\omega'(x)\}^{\frac{1}{2}}}dx\,; \quad n = 2, 3, \ldots, \quad . \quad . \quad (15)$$

together with similar equations for the $\psi$'s.

With these values the series (9) + (11) satisfies formally the conditions of the problem. It remains to be proved that it is the asymptotic expansion, for $k \to \infty$, of that integral of (6) which is determined by the initial values (8). It is unnecessary to work through the detailed analysis; the method consists in forming, by a suitable chain of approximations, a convergent series for the required solution of (6) and showing that we obtain the previous formal solution by taking the asymptotic expansions of the terms in the convergent series. It may suffice to refer * to the solution of a

* J. Horn, Math. Ann. lii. pp. 271 and 340 (1899).

more general equation by this method, and to state that the formal solution is valid for positive values of $x$; consequently, the corresponding solution of (2) is valid for $t>0$ provided we have $b>0$.

It will be seen, from (15), that the expressions for the functions $\phi$ and $\psi$ soon become rather lengthy. Ultimately we shall only require $\phi_0$ and $\psi_0$, but the next two terms have also been calculated so that we may have the expressions for $y$ and $\dot{y}$ up to terms in $k^{-1}$; with the given conditions the series (9) + (11) leads to real series multiplied by $\cos k\omega$ and $\sin k\omega$.

Collecting the various results, we have

$$y\sim\left(1+\frac{1}{x}\right)^{-\frac{1}{4}}\left\{y_0\left(1+\frac{1}{x_0}\right)^{\frac{1}{4}}\cos k\omega + \dot{y}_0\left(\frac{am}{\mathrm{T}}\right)^{\frac{1}{2}}\left(1+\frac{1}{x_0}\right)^{-\frac{1}{4}}\sin k\omega\right\}$$

$$+\frac{1}{k}\left[\tfrac{1}{8}\dot{y}_0\left(\frac{am}{\mathrm{T}}\right)^{\frac{1}{2}}\left(1+\frac{1}{x_0}\right)^{-\frac{1}{4}}\left(1+\frac{1}{x}\right)^{-\frac{1}{4}}\left(\frac{9+12x+8x^2}{6x^{\frac{1}{2}}(1+x)^{\frac{3}{2}}}-\frac{9+12x_0+8x_0^2}{6x_0^{\frac{1}{2}}(1+x_0)^{\frac{3}{2}}}\right)\cos k\omega\right.$$

$$\left.-\left\{\tfrac{1}{8}y_0\left(1+\frac{1}{x_0}\right)^{\frac{1}{4}}\left(1+\frac{1}{x}\right)^{-\frac{1}{4}}\left(\frac{9+12x+8x^2}{6x^{\frac{1}{2}}(1+x)^{\frac{3}{2}}}-\frac{9+12x_0+8x_0^2}{6x_0^{\frac{1}{2}}(1+x_0)^{\frac{3}{2}}}\right)\right.\right.$$

$$\left.\left.+\tfrac{1}{4}y_0x_0^{-2}\left(1+\frac{1}{x_0}\right)^{-\frac{5}{4}}\left(1+\frac{1}{x}\right)^{-\frac{1}{4}}\right\}\sin k\omega\right]+\ldots,\quad .\quad .\quad (16)$$

where $x=(b+vt)/a$; $x_0=b/a$; $k^2=a\mathrm{T}/mv^2$; and

$$\omega=x^{\frac{1}{2}}(1+x)^{\frac{1}{2}}-x_0^{\frac{1}{2}}(1+x_0)^{\frac{1}{2}}-\log\{(1+x)^{\frac{1}{2}}-x^{\frac{1}{2}}\}+\log\{(1+x_0)^{\frac{1}{2}}-x_0^{\frac{1}{2}}\}.\quad (17)$$

We may now write down $\dot{y}$ to the same order, but we shall record only the first terms:

$$\dot{y}\left(\frac{am}{\mathrm{T}}\right)^{\frac{1}{2}}\sim\left(1+\frac{1}{x}\right)^{\frac{1}{4}}\left\{\dot{y}_0\left(\frac{am}{\mathrm{T}}\right)^{\frac{1}{2}}\left(1+\frac{1}{x_0}\right)^{-\frac{1}{4}}\cos k\omega - y_0\left(1+\frac{1}{x_0}\right)^{\frac{1}{4}}\sin k\omega\right\}.\quad (18)$$

4. After this digression on the solution of the equation, which is perhaps of interest in itself, we may return to the dynamical problem.

Before the time $t=0$ we suppose the plate R to be fixed

and the particle to be making simple harmonic vibrations of frequency $n_0$, where

$$n_0 = \left\{\left(\frac{\mathrm{T}}{m}\right).\left(\frac{1}{a}+\frac{1}{b}\right)\right\}^{\frac{1}{2}}.$$

Then the plate is moved with uniform velocity $v$ for a finite distance until the length $b+vt=c$ and is stopped; after this time the particle vibrates with frequency

$$n = \left\{\left(\frac{\mathrm{T}}{m}\right).\left(\frac{1}{a}+\frac{1}{c}\right)\right\}^{\frac{1}{2}}.$$

If $v$ is small, so that $k$ is large, the values of $y$ and $\dot{y}$ when the plate is stopped are given by (16) and (18). It seems permissible to neglect any impulsive changes which might be supposed to occur at the starting and stopping of the plate, because of the idealized nature of the apparatus; the string is such that its inertia may be neglected, and further, that its tension is instantaneously adjusted to the constant value T.

With $v$ small, we may take the first terms in (16) and (17), and we have for the energy after the displacement

$$\begin{aligned}\mathrm{E} &= \tfrac{1}{2}m\dot{y}^2+\tfrac{1}{2}\mathrm{T}y^2(a^{-1}+c^{-1}),\\ &\sim \frac{1}{2}\frac{\mathrm{T}}{a}\left(1+\frac{a}{c}\right)^{\frac{1}{2}}\left\{\dot{y}_0{}^2\left(\frac{am}{\mathrm{T}}\right)\left(1+\frac{a}{b}\right)^{-\frac{1}{2}}+y_0{}^2\left(1+\frac{a}{b}\right)^{\frac{1}{2}}\right\},\\ &\sim \left(\frac{1}{a}+\frac{1}{c}\right)^{\frac{1}{2}}\left(\frac{1}{a}+\frac{1}{b}\right)^{-\frac{1}{2}}\mathrm{E}_0.\end{aligned}$$

Hence we have

$$\mathrm{E}/n \sim \mathrm{E}_0/n_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

5. As a particular case of this problem, suppose the particle to move between smooth guides through C at right angles to CR; for small motions this is analytically similar to the Rayleigh pendulum, a simple pendulum swinging under gravity with the length altering at a uniform rate. The equation of motion, with the same notation as before, is

$$(b+vt)\frac{d^2y}{dt^2}+\frac{\mathrm{T}}{m}y = 0. \quad . \quad . \quad . \quad . \quad (20)$$

The complete solution of this equation is

$$y = x^{\frac{1}{2}}\{\mathrm{AJ}_1(2kx^{\frac{1}{2}})+\mathrm{BN}_1(2kx^{\frac{1}{2}})\}, \quad . \quad . \quad (21)$$

where $x=b+vt$; $k^2=\mathrm{T}/mv^2$.

We have also

$$\dot{y} = vy' = kv\{AJ_0(2kx^{\frac{1}{2}}) + BN_0(2kx^{\frac{1}{2}})\}. \quad . \quad (22)$$

Using the formula

$$J_1(x)N_0(x) - J_0(x)N_1(x) = 2/\pi x,$$

we have

$$A = (\pi/v)\{kvy_0N_0(2kb^{\frac{1}{2}}) - b^{\frac{1}{2}}\dot{y}_0N_1(2kb^{\frac{1}{2}})\},$$

$$B = (\pi/v)\{b^{\frac{1}{2}}\dot{y}_0J_1(2kb^{\frac{1}{2}}) - kvy_0J_0(2kb^{\frac{1}{2}})\}. \quad . \quad . \quad (23)$$

Suppose now that

$$\left.\begin{aligned} y &= C_0 \sin(n_0t + \alpha_0), \quad \text{for } t < 0, \\ y &= C \sin(nt + \alpha), \quad \text{for } t > (c-b)/v, \end{aligned}\right\} \quad . \quad (24)$$

while for the intervening time, $y$ is given by (21); in (24) we have $n_0 = kv/b^{\frac{1}{2}}$, $n = kv/c^{\frac{1}{2}}$.

After a little reduction we obtain

$$C \sin\{k(c-b)c^{-\frac{1}{2}} + \alpha\} = c^{\frac{1}{2}}\{AJ_1(2kc^{\frac{1}{2}}) + BN_1(2kc^{\frac{1}{2}})\},$$

$$C \cos\{k(c-b)c^{-\frac{1}{2}} + \alpha\} = c^{\frac{1}{2}}\{AJ_0(2kc^{\frac{1}{2}}) + BN_0(2kc^{\frac{1}{2}})\}. \quad (25)$$

With $v$ small so that the transformation is made slowly, we may use the first terms in the asymptotic expansions of the Bessel functions, namely

$$\sqrt{\tfrac{1}{2}\pi u}\, J_0(u) \sim \cos(u - \tfrac{1}{4}\pi); \quad \sqrt{\tfrac{1}{2}\pi u}\, N_0(u) \sim \sin(u - \tfrac{1}{4}\pi);$$

$$\sqrt{\tfrac{1}{2}\pi u}\, J_1(u) \sim \sin(u - \tfrac{1}{4}\pi); \quad \sqrt{\tfrac{1}{2}\pi u}\, N_1(u) \sim -\cos(u - \tfrac{1}{4}\pi).$$

From (23) we find

$$A \sim \sqrt{(\pi k/b^{\frac{1}{2}})}C_0 \cos\left(2kb^{\frac{1}{2}} - \frac{\pi}{4} - \alpha_0\right),$$

$$B \sim \sqrt{(\pi k/b^{\frac{1}{2}})}C_0 \sin\left(2kb^{\frac{1}{2}} - \frac{\pi}{4} - \alpha_0\right). \quad . \quad . \quad (26)$$

With a similar reduction (25) now gives

$$C \begin{matrix}\sin \\ \cos\end{matrix}\left\{\frac{k(c-b)}{c^{\frac{1}{2}}} + \alpha\right\} \sim \frac{c^{\frac{1}{4}}}{b^{\frac{1}{4}}}C_0 \begin{matrix}\sin \\ \cos\end{matrix}\left\{2k(c^{\frac{1}{2}} - b^{\frac{1}{2}}) + \alpha_0\right\}. \quad (27)$$

Thus the change in the amplitude of the vibration by this slow transformation follows the law

$$C/C_0 \sim (c/b)^{\frac{1}{4}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and since the energy is proportional to the square of the amplitude and inversely proportional to the length of string, the adiabatic invariance of $E/n$ follows from this result.

*Vibration of Uniform String.*

6. With T as the tension of the string and $\rho$ the line density, the equation of motion is

$$\frac{\partial^2 y}{\partial t^2} = c^2 \frac{\partial^2 y}{\partial x^2}; \quad c^2 = \mathrm{T}/\rho. \quad . \quad . \quad . \quad . \quad (29)$$

The density of energy per unit length is given by

$$e = \tfrac{1}{2}\rho(\partial y/\partial t)^2 + \tfrac{1}{2}\mathrm{T}(\partial y/\partial x)^2. \quad . \quad . \quad . \quad (30)$$

Now suppose that the motion of the infinite string is such that the origin O is a fixed node and the point R given by $x = a + vt$ is a node moving with uniform velocity $v$. The rate of increase of energy E in the portion OR of the string is

$$\frac{\partial \mathrm{E}}{\partial t} = \frac{\partial}{\partial t}\int_0^{a+vt} e\, dx = ve_{\mathrm{R}} + \int_0^{a+vt} \frac{\partial e}{\partial t}\, dx. \quad . \quad . \quad (31)$$

After a partial integration, using (29) and (30) and the condition $y = 0$ at O, this leads to

$$\frac{\partial \mathrm{E}}{\partial t} = ve_{\mathrm{R}} + \mathrm{T}\left(\dot{y}\frac{\partial y}{\partial x}\right)_{\mathrm{R}}. \quad . \quad . \quad . \quad . \quad (32)$$

But the kinematic condition at the travelling node is

$$\dot{y} + v\frac{\partial y}{\partial x} = 0. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Hence we have

$$e_{\mathrm{R}} = \tfrac{1}{2}\rho(c^2 + v^2)(\partial y/\partial x)^2_{\mathrm{R}},$$

$$\partial \mathrm{E}/\partial t = ve_{\mathrm{R}} - \rho c^2 v(\partial y/\partial x)^2_{\mathrm{R}} = \tfrac{1}{2}v\rho(v^2 - c^2)(\partial y/\partial x)^2_{\mathrm{R}}.$$

If we think of the travelling node R as produced by an ideal perfect reflector moving with velocity $v$, the equivalent pressure of the vibrations at R is then

$$p = -\frac{1}{v}\frac{\partial \mathrm{E}}{\partial t} = \frac{c^2 - v^2}{c^2 + v^2} e_{\mathrm{R}}. \quad . \quad . \quad . \quad . \quad (34)$$

We notice incidentally that if we picture the reflector in this case as a plate with a small hole through which the string passes, the pressure $p$ so calculated is less than the resolved statical tension of the string if we assume the string undisturbed beyond the plate; for the latter force, being $\frac{1}{2}\mathrm{T}(\partial y/\partial x)^2_{\mathrm{R}}$, is equal to $c^2 e_{\mathrm{R}}/(c^2 + v^2)$.

The result (34) is Larmor's formula generalized, without

being confined to simple harmonic waves and average values of the quantities involved.

7. The general solution of (29) is

$$y = f(ct-x)+\mathrm{F}(ct+x), \quad . \quad . \quad . \quad . \quad (35)$$

and the boundary conditions are $y=0$ for $x=0$ and for $x=a+vt$. Hence the motion is given by

$$y = f(ct-x)-f(ct+x), \quad . \quad . \quad . \quad . \quad (36)$$

where $f$ satisfies the functional equation

$$f\{(c-v)t-a\} = f\{(c+v)t+a\}. \quad . \quad . \quad . \quad (37)$$

We have now

$$e_{\mathrm{R}} = \rho c^2[f'^2\{(c-v)t-a\}+f'^2\{(c+v)t+a\}]$$
$$= \frac{2\rho c^2(c^2+v^2)}{(c+v)^2} f'^2\{(c-v)t-a\},$$

$$\left(\dot{y}\frac{\partial y}{\partial x}\right)_{\mathrm{R}} = c[f'^2\{(c-v)t-a\}-f'^2\{(c+v)t+a\}]$$
$$= -\frac{4c^2v}{(c+v)^2} f'^2\{(c-v)t-a\}.$$

Substituting in (32), we deduce again the result (34).

8. We may examine some particular solutions of the functional equation (37). It is of the form

$$f(\alpha u+\beta) = f(u), \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where $\alpha=(c+v)/(c-v)$ and $\beta=2ac/(c-v)$.

If we write

$$\left.\begin{aligned} f(u) &= \phi(\xi), \quad f(\alpha u+\beta) = \phi(\xi+1), \\ u &= \psi(\xi), \qquad \alpha u+\beta = \psi(\xi+1), \end{aligned}\right\} \quad . \quad . \quad (39)$$

then (38) is replaced by the pair of difference equations

$$\left.\begin{aligned} \phi(\xi+1)-\phi(\xi) &= 0, \\ \psi(\xi+1)-\alpha\psi(\xi) &= \beta. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (40)$$

Solutions of these are obtained by the ordinary rules for difference equations; and so we arrive at solutions of (38) by eliminating $\xi$ from

$$\left.\begin{aligned} f(u) &= \phi(\xi), \\ u = \psi(\xi) &= \frac{\beta}{1-\alpha}+\alpha^{\xi}\chi(\xi), \end{aligned}\right\} \quad . \quad . \quad (41)$$

where $\phi$ and $\chi$ are arbitrary periodic functions of $\xi$ of unit period. In particular, if we take

$$\phi(\xi) = \mathrm{A}\sin 2s\pi\xi, \quad \chi(\xi) = -\beta/(1-\alpha),$$

where $s$ is an integer, we have

$$f(u) = \mathrm{A}\sin\left[2s\pi\frac{\log\{1-u(1-\alpha)/\beta\}}{\log\alpha}\right]. \quad . \quad (42)$$

Returning now to (36), and replacing the values of $\alpha$ and $\beta$, we have a motion of the vibrating string such that there is a stationary node O at $x=0$ and a travelling node R at $x=a+vt$, namely

$$y = \mathrm{A}\sin 2s\pi\frac{\log\{1+v(ct+x)/ca\}}{\log\{(c+v)/(c-v)\}} - \mathrm{A}\sin 2s\pi\frac{\log\{1+v(ct-x)/ca\}}{\log\{(c+v)/(c-v)\}}. \quad . \quad (43)$$

It may be easily verified that the limiting value of this expression for $v\to 0$ is the ordinary case of steady vibrations,

$$y = 2\mathrm{A}\sin\frac{s\pi x}{a}\cos\frac{s\pi ct}{a}. \quad . \quad . \quad . \quad . \quad . \quad (44)$$

The expression (43) may be used to examine the motion of the string between O and R, assuming $a$ and $t$ both positive, for various ratios of $v$ to $c$.

9. It is unnecessary to repeat the calculation for the pressure of the vibrations at R, as the particular case is included in the general formulæ of § 7.

We shall not attempt to solve the general problem of the finite motion of the reflecting plate R, as was done in § 4 for the simple particle. It would mean starting with R fixed and the string performing some normal vibration ; the plate R would then be moved with uniform velocity through a certain distance and stopped. We should have to fit given initial conditions by a general solution, possibly made up of a series of expressions like (43). Further, we should have to consider the possibility of impulsive disturbances at the beginning and end of the motion, which would require a closer specification of the action of the plate ; it may be presumed that such disturbances would be narrow pulses emitted from R at a sudden change in velocity. We are concerned chiefly with the results when $v$ is small ; and as (43) approximates then to a normal vibration, we shall calculate from it the change

in the energy as the length of the string increases from $a$ to $b$.

Making use of the general formulæ in § 7, we have

$$\mathrm{E}_b - \mathrm{E}_a = -\frac{2\rho c^2(c-v)}{c+v}\int_0^{t(b-a)/v} [f'\{(c-v)t-a\}]^2 dt, \quad (45)$$

where

$$f'(u) = \mathrm{A}\sin\left\{2s\pi\log\left(1+\frac{vu}{ca}\right)/\log\frac{c+v}{c-v}\right\}. \quad (46)$$

Putting $a+vt=l$, this gives

$$\mathrm{E}_b - \mathrm{E}_a = -\frac{8s^2\pi^2v^2c^2\rho}{(c^2-v^2)\{\log(c+v)/(c-v)\}^2} \times \int_a^b \cos^2\left[2s\pi\frac{\log\{(c-v)l/ca\}}{\log\{(c+v)/(c-v)\}}\right]dl. \quad (47)$$

If $\theta$ is the angle under the integral sign, and if $\alpha$ is written for $\log(c+v)/(c-v)$, the value of the integral is one-half of

$$\frac{1}{a}-\frac{1}{b}+\frac{4s\pi\alpha}{16s^2\pi^2+\alpha^2}\left\{\frac{1}{b}\sin 2\theta_b - \frac{1}{a}\sin 2\theta_a\right\} - \frac{\alpha^2}{16s^2\pi^2+\alpha^2}\left\{\frac{1}{b}\cos 2\theta_b - \frac{1}{a}\cos 2\theta_a\right\}.$$

Collecting the results, and expanding, we have

$$\mathrm{E}_b - \mathrm{E}_a = -s^2\pi^2c^2\rho\left[\frac{1}{a}-\frac{1}{b}+\frac{v}{2s\pi cb}\sin\left(\frac{2s\pi c}{v}\log\frac{b}{a}\right)+\ldots\right]. \quad (48)$$

Thus as $v\to 0$, we have

$$\mathrm{E}_b - \mathrm{E}_a \sim -s^2\pi^2c^2\rho\left(\frac{1}{a}-\frac{1}{b}\right).$$

But, to the same approximation, we have from (44), $\mathrm{E}_a = s^2\pi^2c^2\rho/a$; thus

$$b\,\mathrm{E}_b \sim a\,\mathrm{E}_a.$$

Since the frequency of a normal vibration is inversely proportional to the length of string, this is the required adiabatic invariance of $\mathrm{E}/n$.

### *Electromagnetic Waves.*

10. The preceding analysis can be applied directly to electrical vibrations in free space. We shall confine our attention to plane waves with wave fronts perpendicular

to $Ox$; if E and H are the electric and magnetic vectors,

$$e = \tfrac{1}{2}\mathrm{E}^2 + \tfrac{1}{2}\mathrm{H}^2,$$

and the equation for flow of energy is

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x}(c\mathrm{EH}) = 0. \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Consider a disturbance for which the point O is a stationary node for E, and the point R a travelling node for $\mathrm{E} - v\mathrm{H}/c$; so that

$$\mathrm{E} = 0 \text{ for } x = 0; \quad \mathrm{E} - \frac{v}{c}\mathrm{H} = 0 \text{ for } x = a + vt. \quad (50)$$

Then the rate of increase of energy in the region OR is

$$\frac{\partial}{\partial t}\int_0^{a+vt} e\,dx = ve_{\mathrm{R}} - c(\mathrm{EH})_{\mathrm{R}} = -\tfrac{1}{2}v\left(1 - \frac{v^2}{c^2}\right)\mathrm{H}_{\mathrm{R}}^2, \quad (51)$$

since

$$e_{\mathrm{R}} = \tfrac{1}{2}v\left(1 + \frac{v^2}{c^2}\right)\mathrm{H}_{\mathrm{R}}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Hence, if this nodal condition is the boundary condition for an ideal perfect reflector in motion, the corresponding pressure of the vibrations is $(c^2 - v^2)e_{\mathrm{R}}/(c^2 + v^2)$; this, of course, agrees with the usual calculation from electrodynamic theory for the mechanical force on the reflector.

If we have a fixed perfect conductor at the plane $x = 0$ and a moving perfect conductor at $x = a + vt$, then plane disturbances in the region between them are given by

$$\left.\begin{aligned} \mathrm{E} &= f(ct - x) - f(ct + x), \\ \mathrm{H} &= f(ct - x) + f(ct + x), \end{aligned}\right\} \quad . \quad . \quad . \quad (53)$$

where $f$ satisfies the functional equation

$$(c - v)f\{(c - v)t - a\} = (c + v)f\{(c + v)t + a\}.$$

These satisfy the equations and the conditions (50). Referring back to equations (38)–(42), particular types of solution can be written down; for instance, we may take, in (53),

$$f(u) = \frac{1}{ca + vu}\sin\left[2s\pi\frac{\log(1 + vu/ca)}{\log\, c + v)/(c - v)}\right]. \quad . \quad (54)$$

With the help of these solutions one might study in detail the problems of the previous sections; for instance, the change produced in a steady normal vibration between two fixed planes if one of the planes is moved with uniform velocity through a finite distance and then stopped.

*Dispersive Medium and Group Velocity.*

11. As a simple case of a dispersive medium we consider the transverse vibrations of a uniform string, at constant tension T, each particle of which is attracted to its equilibrium position by a force proportional to displacement *.

The equation of motion is of the form

$$\frac{\partial^2 y}{\partial t^2} - c^2 \frac{\partial^2 y}{\partial x^2} + n^2 y = 0, \quad . \quad . \quad . \quad . \quad (55)$$

with $c^2 = \mathrm{T}/\rho$; the energy density is

$$e = \tfrac{1}{2}\rho(\dot{y}^2 + c^2 y'^2 + n^2 y^2); \quad . \quad . \quad . \quad . \quad (56)$$

while the flow of energy is given by

$$\frac{\partial e}{\partial t} - \frac{\partial}{\partial x}\left(\mathrm{T}\dot{y}\frac{\partial y}{\partial x}\right) = 0. \quad . \quad . \quad . \quad . \quad (57)$$

If there is a stationary node at O, and a travelling node at R, so that

$$\dot{y} + v y' = 0, \text{ for } x = a + vt,$$

then by the same process as before, from the rate of decrease of energy in OR, we find

$$p = \tfrac{1}{2}\rho(c^2 - v^2)\left(\frac{\partial y}{\partial x}\right)_{\mathrm{R}}^2 = \frac{c^2 - v^2}{c^2 + v^2} e_{\mathrm{R}}. \quad . \quad . \quad (58)$$

It appears that Larmor's expression has a still wider application in that it may include dispersive media. We may verify this conclusion for simple harmonic waves.

Suppose there are forward and backward waves of equal amplitude and adjusted so that there is a node R travelling with velocity $v$; there is now no stationary node.

We have

$$y = \sin\kappa_1(\mathrm{V}_1 t - x) - \sin\kappa_2(\mathrm{V}_2 t + x), \quad . \quad . \quad (59)$$

where the wave velocity V is given by

$$\kappa \mathrm{V} = \surd(\kappa^2 c^2 + n^2). \quad . \quad . \quad . \quad . \quad . \quad (60)$$

If we take the travelling node to be at $x = vt$, we have

$$(\kappa_2{}^2 c^2 + n^2)^{\frac{1}{2}} + \kappa_2 v = (\kappa_1{}^2 c^2 + n^2)^{\frac{1}{2}} - \kappa_1 v. \quad . \quad . \quad (61)$$

Thus the wave-length of the reflected wave is found from

$$\kappa_2 = \frac{\kappa_1(c^2 + v^2) - 2v(\kappa_1{}^2 c^2 + n^2)^{\frac{1}{2}}}{c^2 - v^2}. \quad . \quad . \quad . \quad (62)$$

* "The Propagation of Disturbances in Dispersive Media," Camb. Tracts, No. 17, p. 58 (1914).

There is no fixed node; but we may consider the rate of increase of energy between the fixed point O and the moving point R. It is

$$\frac{\partial}{\partial t}\int_0^{vt} e\,dx = re_{\mathrm{R}} + \mathrm{T}\left(\dot{y}\frac{\partial y}{\partial x}\right)_{\mathrm{R}} - \mathrm{T}\left(\dot{y}\frac{\partial y}{\partial x}\right)_0 . \quad . \quad (63)$$

The last term represents the rate of work of the tension at O upon the medium outside the range OR; and therefore, as before, we consider the equivalent pressure of radiation at R to be given by

$$-p = e_{\mathrm{R}} + \frac{\mathrm{T}}{v}\left(\dot{y}\frac{\partial y}{\partial x}\right)_{\mathrm{R}} . \quad . \quad . \quad . \quad (64)$$

From (56), (59), and (62), if we write

$$\kappa_2(\mathrm{V}_2 - v)t = \kappa_1(\mathrm{V}_1 + v)t = \alpha, \quad . \quad . \quad . \quad (65)$$

we obtain

$$\begin{aligned} e_{\mathrm{R}} &= \tfrac{1}{2}\rho(c^2+v^2)(\kappa_1+\kappa_2)^2\cos^2\alpha \\ &= 2\rho\frac{c^2+v^2}{(c^2-v^2)^2}\{\kappa_1 c^2 - v(\kappa_1^2c^2+n^2)^{\frac{1}{2}}\}^2\cos^2\alpha, \quad (66) \end{aligned}$$

$$\left(\dot{y}\frac{\partial y}{\partial x}\right)_{\mathrm{R}} = -\frac{4v}{(c^2-v^2)^2}\{\kappa_1 c^2 - v(\kappa_1^2c^2+n^2)^{\frac{1}{2}}\}^2\cos^2\alpha. \quad (67)$$

Hence the equivalent pressure is

$$p = \frac{2\rho}{c^2-v^2}\{\kappa_1 c^2 - v(\kappa_1^2c^2+n^2)^{\frac{1}{2}}\}^2\cos^2\alpha = \frac{c^2-v^2}{c^2+v^2}e_{\mathrm{R}}. \quad (68)$$

It will be noticed that the pressure is proportional to $(\mathrm{U}_1 - v)^2$, where $\mathrm{U}_1$ is the group velocity of the incident wave; for

$$\mathrm{U} = \frac{d(\kappa \mathrm{V})}{d\kappa} = \frac{\kappa c^2}{(\kappa^2c^2+n^2)^{\frac{1}{2}}} . \quad . \quad . \quad . \quad (69)$$

But the connexion with group velocity is more direct when we consider the streams of energy in the incident and reflected waves. It must be remembered that in such a treatment we are dealing with average values; for instance, group velocity for a simple harmonic train is the average rate of flow of energy. Larmor's method of obtaining his formula for the uniform non-dispersive string was to consider the rate of increase of energy as due on the average to the streams of energy through the travelling node; thus it

was given by $e_2(c+v)-e_1(c-v)$, with $e_1$ and $e_2$ as the average energy densities in the two wave-trains.

In the present dispersive case, we should have by a similar argument for average values

$$p = -\frac{1}{v}\{e_2(U_2+v)-e_1(U_1-v)\}. \quad . \quad . \quad . \quad (70)$$

But we have

$$\bar{e} = \tfrac{1}{2}\rho(\kappa^2c^2+n^2). \quad . \quad . \quad . \quad . \quad . \quad (71)$$

From (62), (69), (70), and (71) after a little reduction, we get

$$\bar{p} = \frac{\rho}{c^2-v^2}\{\kappa_1c^2-v(\kappa_1^2c^2+n^2)^{\frac{1}{2}}\}^2, \quad . \quad . \quad . \quad (72)$$

which is just the average value of the previous expression (68).

In the same way we may remove an apparent discrepancy. It follows from (68) with $v=0$ that $p=e_R$; that is, the pressure of radiation on a stationary reflector is equal to the energy density in front of the reflector. On the other hand, the usual statement, originally made by Rayleigh * and since elaborated by others, is that for a dispersive medium

$$p = \frac{U}{V}e. \quad . \quad . \quad . \quad . \quad . \quad . \quad (73)$$

From the introduction of group velocity it is obvious that in (73) we are dealing only with simple harmonic waves and with average values; in fact, $e$ is not the energy density immediately in front of the reflector, but is the average density for simple waves over the whole range of the medium in front of the reflector. Now for a reflector at rest, the reflected wave has the same wave-length as the incident, so from (71)

$$\bar{e} = \rho(\kappa^2c^2+n^2), \quad . \quad . \quad . \quad . \quad . \quad (74)$$

where the average is with respect to time and position.

Further, immediately in front of the reflector, for $v=0$, from (66)

$$e_R = \rho\kappa^2c^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

where the average with respect to time is taken.

* Rayleigh, Phil. Mag. 1902, or 'Scientific Papers,' v. p. 47.

Since from (60) and (69)

$$U/V = \kappa^2 c^2/(\kappa^2 c^2 + n^2),$$

it follows that (73) is consistent with (68) for $v=0$. It is, however, only a particular case, for average values; the more general statement is that the pressure is equal to the energy density immediately in front of the stationary reflector.

Whether these results are peculiar to the special medium studied here must be left for further investigation, as well as some interesting questions which arise when the velocity of the reflector is greater than the group velocity of the incident waves or even greater than the velocity of the front of a limited disturbance.

## *Summary.*

The paper contains a study of the solution of the following type of problem, with various applications: the small transverse vibrations of a string stretched at constant tension, one end being fixed and the other passing through a small hole in a plate which moves along the string with uniform velocity $v$.

1. With a single particle attached to a light string, the equation of motion is solved and an asymptotic expansion found when $v$ is small; this is applied to the adiabatic invariance of $E/n$, where E is energy and $n$ frequency. A particular case corresponds to the Rayleigh pendulum.

2. With a uniform string, solutions are found which give a stationary node and a travelling node, and similar applications are made.

The pressure of radiation at a moving reflector is examined and the formula $p=(c^2-v^2)e/(c^2+v^2)$ is generalized.

3. Similar solutions are indicated for plane electromagnetic waves between fixed and moving planes which are perfect reflectors.

4. When the string is endowed with a certain dispersive property, the pressure of radiation is found to obey the same general formula, and the relation of this to the usual formulæ involving group velocity is shown.

# LXXI. *The Relation between the Refractivities and the Sizes of the Atoms of Certain Elements.* By J. E. Calthrop, *B.A. (Cantab.), B.Sc. (Lond.)* *.

## I. *Introduction.*

THE relation between the refractivities and the atomic weights of certain elements has been investigated by Cuthbertson †, who found that the values of $(\mu_D - 1) \times 10^6$, where $\mu_D$ is the refractive index for sodium light, were for the elements of a vertical column of the Periodic Table proportional to integers.

For example, in the case of the inert gases the following results were obtained :—

| Element. | $(\mu_D - 1) \times 10^6$. | Ratio. |
|---|---|---|
| He ..... | 34·9 | 1 |
| Ne ..... | 68·7 | 2 |
| Ar ..... | 283·7 | 8 |
| Kr ..... | 427·3 | 12 |
| Xe ..... | 702·0 | 20 |

The same ratios were approximately obtained for Groups V., VI., and VII., although in certain cases the discrepancy from this whole number relation was as much as 8–17 per cent.

$(\mu_D - 1) \times 10^6$ was seen to increase with atomic weight in any vertical column, and to decrease with atomic weight in a horizontal row.

Le Bas ‡ has also investigated the regularities of these elements, and has given tables of combined atomic refractivities and of atomic volumes, but the atomic volumes given do not agree with those of Stefan Meyer §. In some cases mean values were given, as the atomic volume depends on the condition of the substance.

The following is the table of atomic volumes as given by Le Bas :—

| | | | |
|---|---|---|---|
| C. | N. | O. | F. |
| 14·8 | 12·0 | 7·4 | 6·5 |
| Si. | P. | S. | Cl. |
| 30·0 | 27·0 | 23·5 | 21·6 |
| | | | Br. |
| | | | 29·0 |
| | | | I. |
| | | | 37·0 |

* Communicated by Prof. C. H. Lees, D.Sc., F.R.S.

† Science Progress, No. 10, iii. p. 283 (Oct. 1908).

‡ 'Nature,' cviii. p. 272 (Oct. 1921).

§ Sommerfeld, 'Atomic Structure,' 1922.

For I, N, and S, mean values were taken.

The following was his table of combined atomic refractivities, where the formula for refractivity was of the Lorentz form :— $\frac{\mu_D^2-1}{\mu_D^2+2}\cdot\frac{A}{\rho}$, where A is the atomic weight and $\rho$ the density :—

| | | | |
|---|---|---|---|
| C. | N. | O. | F. |
| 3·36 | 2·38 | 1·48 | 0·67 |
| Si. | P. | S. | Cl. |
| 8·80 | 7·76 | 6·79 | 5·96 |
| | As. | Se. | Br. |
| | 10·50 | 9·89 | 8·79 |
| | | | I. |
| | | | 13·87 |

From these data Le Bas found differences in the atomic refractivities which correspond to differences in the atomic volumes. Plotting atomic refractivities against atomic volumes he found an approximately linear relation.

He therefore concluded that the atomic refractivities were proportional to the atomic volumes, and also stated that the former were roughly proportional to the valencies in any horizontal row of the Periodic Table. Little mention was made of the inert gases as fitting into this scheme, because of course the combining values of the atomic refractivities are derived from compounds.

## II. *Relation between Refractivity and Atomic Size.*

The aim of the present paper is to show that there is an intimate connexion between the refractivities and atomic sizes of a number of gases and vapours. The atomic sizes or volumes are calculated from the results of Prof. W. L. Bragg *, and the term size is employed so that there is no confusion with the usual meaning of atomic volume as employed by Meyer.

Professor Bragg gave a comprehensive list of atomic diameters, and when these are plotted against the atomic numbers, curves showing periodicity similar to those of Meyer's are obtained. In the 4th edition of their 'X-rays and Crystal Structure' the authors, W. H. & W. L. Bragg, prefer the term "combination radius" and emphasize the limitations of the meaning of "atomic diameter." The diameters of the atoms of the inert gases could not, of course, be measured from experiments on crystal structure,

* W. L. Bragg, Phil. Mag. xl. p. 169 (1920).

but could be inferred from the positions of these elements in the table. As no value for phosphorus was given, this has been estimated as 1·03 Å for the purposes of the present paper. It cannot be very different from those of sulphur, chlorine, and argon in the same row of the Periodic Table. We therefore take the mean of S 1·02 Å, Cl 1·05 Å, and Ar 1·025 Å, and use 1·03 Å for phosphorus. All the other values used in the following tables are those given in Prof. Bragg's paper.

The refractivities are those from which Cuthbertson derived his simple ratios, and they may be found in his original paper.

## III. *Data and Results.*

The elements examined fall in the following part of the Periodic Table :—

| No. of row. | Groups I., II., III., IV. | V. | VI. | VII. | VIII. | 0. |
|---|---|---|---|---|---|---|
| 1 ..... | 1 H | .. | ... | ... | ... | 2 He |
| 2 ..... | ... | 7 N | 8 O | 9 F | ... | 10 Ne |
| 3 ..... | ... | 15 P | 16 S | 17 Cl | ... | 18 Ar |
| 4 *a*..... | ... | — | — | — | ... | — |
| 4 *b*..... | ... | 33 As | 34 Se | 35 Br | ... | 36 Kr |
| 5 *a*..... | ... | — | — | — | ... | — |
| 5 *b*..... | ... | ... | 52 Te | 53 I | ... | 54 Xe |

The various quantities are set out in the following tables. The atomic radius is in Ångström units, $10^{-10}$ metre, the volume in cubic Ångström units, and $\mu_D$ refers to sodium light :—

| Element. | At. radius $r$. | $\frac{4}{3}\pi r^3$. | $(\mu_D-1)\times 10^6$. | ref./vol. |
|---|---|---|---|---|
| Ne ..... | 0·650 Å | 1·150 | 68·7 | 59·71 |
| Ar ..... | 1·025 „ | 4·512 | 283·7 | 62·87 |
| Kr ..... | 1·175 „ | 6·800 | 427·3 | 62·83 |
| Xe ..... | 1·350 „ | 10·310 | 702·0 | 68·11 |
| | | | Mean..... | 63·38 |

*Results for Column VII.*

| Element. | At. radius $r$. | $\frac{4}{3}\pi r^3$. | $(\mu_D-1)\times 10^6$. | ref./vol. |
|---|---|---|---|---|
| F..... | 0·67 Å | 1·261 | 195·0 | 154·6 |
| Cl ..... | 1·05 „ | 4·852 | 768·0 | 158·3 |
| Br ..... | 1·19 „ | 7·060 | 1125·0 | 159·3 |
| I ..... | 1·40 | 11·50 | 1920($v$)–2050($r$)* | 167·0–214·4 |
| | | | Mean of first 3 ... | 157·4 |

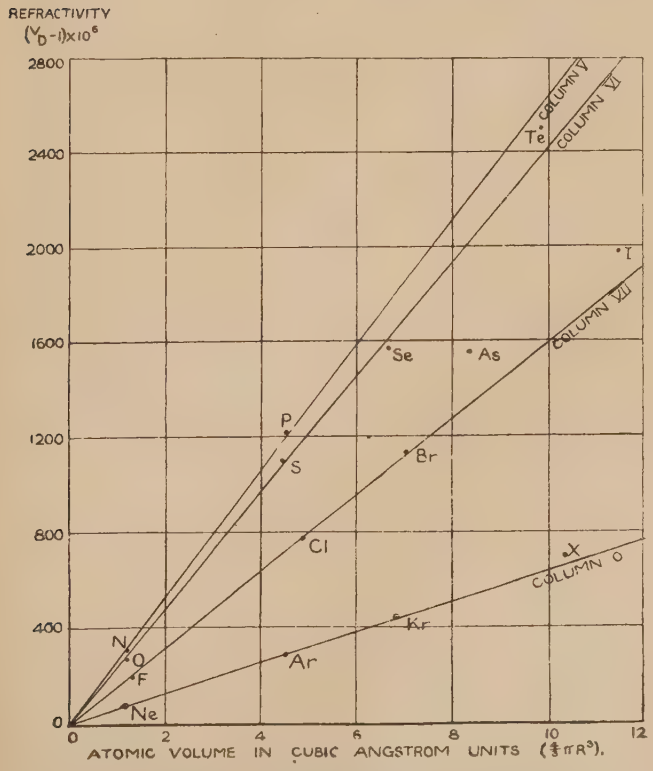
* Results of Hurion for violet and red light.

*Results for Column VI.*

| Element. | At. radius $r$. | $\frac{4}{3}\pi r^3$. | $(\mu_D-1)\times10^6$. | ref./vol. |
|---|---|---|---|---|
| O..... | 0·65 Å | 1·152 | 270·2 | 234·5 |
| S..... | 1·02 ,, | 4·445 | 1101·0 | 247·6 |
| Se ..... | 1·17 ,, | 6·711 | 1565·0 | 233·2 |
| Te ..... | 1·33 ,, | 9·860 | 2495·0 | 253·0 |
| | | | Mean..... ..... | 242·1 |

*Results for Column V.*

| Element. | At. radius $r$. | $\frac{4}{3}\pi r^3$. | $(\mu_D-1)\times10^6$. | ref./vol. |
|---|---|---|---|---|
| N..... | 0·65 Å | 1·152 | 297·1 | 257·9 |
| P..... | 1·03 ,, | 4·577 | 1212·0 | 264·8 |
| As ..... | 1·26 , | 8·383 | 1552·0 | 185·1 |
| | | | Mean of first 2... | 261·4 |




Curves showing the relation between refractivity and atomic volume.

It will be seen that in most cases the ratio of refractivity to the volume is constant in any vertical column, with considerable accuracy.

Arsenic does not seem to fit in the scheme at all well. In the diagram the refractivities and atomic sizes (volumes) are plotted, and give straight lines with slight discrepancies for xenon, iodine, and tellurium. In spite of these it is reasonable to conclude that the refractivities of the elements in a vertical column of the Periodic Table are proportional to the atomic volumes, but that the constant of proportionality is different from column to column.

It is interesting to see how the ratios of the atomic volumes accord with the simple whole number of Cuthbertson and with the actual ratio of the refractivities.

In the following tables we therefore take the first member as 2, and express the others on this basis :—

*Column* 0.

| Element. | Ratio of volumes. | Ratio of refractivities. | Cuthbertson's number. |
|---|---|---|---|
| Ne ..... | 2 | 2 | 2 |
| Ar ..... | 7·85 | 8·26 | 8 |
| Kr ..... | 11·82 | 12·44 | 12 |
| Xe ..... | 17·93 | 20·43 | 20 |

*Column VII.*

| | | | |
|---|---|---|---|
| F ..... | 2 | 2 | 2 |
| Cl ..... | 7·70 | 7·88 | 8 |
| Br ..... | 11·12 | 11·54 | 12 |
| I ..... | 18·24 | 19·69–21·03 | 20 |

*Column VI.*

| | | | |
|---|---|---|---|
| O ..... | 2 | 2 | 2 |
| S ..... | 7·72 | 8·15 | 8 |
| Se ..... | 11·65 | 11·58 | 12 |
| Te ..... | 17·12 | 18·47 | 20 |

*Column V.*

| | | | |
|---|---|---|---|
| N ..... | 2 | 2 | 2 |
| P ..... | 7·94 | 8·16 | 8 |
| As ..... | 14·56 | 10·45 | 12 |

There is very fair agreement between the ratios of the volumes and the ratios of the refractivities of the first

three members of a column, but the agreement for xenon, iodine, tellurium, and arsenic is not so good. A possible explanation of an approximately whole number relation such as the one suggested by Cuthbertson, is that the atomic radii of elements towards the end of a period tend to a minimum and have approximately the same value. There remains the difficulty, however, that the ratios ref./vol. are not the same for all columns.

## IV. *Suggested Explanation of Discrepancies.*

A small error in the radius produces a much larger error in the volume. Thus an increase of only 4 per cent. in the radius of xenon and iodine and of 1·2 per cent. in that of tellurium would give excellent agreement with the numbers derived from the refractivities of these elements. Bragg's values are for crystals, and it is possible that in the state of gas or vapour the radii are slightly larger than the values occurring in crystals. Thus, for example, Schwendenwein *, employing the dynamic model of A. Landé, finds a radius for iodine of 1·432 Å, which is larger than Bragg's value by about the amount demanded.

This value gives a volume of 12·30 cubic Ångström units, a value for $\frac{\text{refractivity}}{\text{volume}}$ of 159·7–166·7 (instead of 157·4 for the other elements of the column), and a value corresponding to Cuthbertson's 20 of 19·51.

Other methods of determining atomic diameters such as those of Rankine from viscosity measurements, of Richards from compressibilities, and of Landé's work on atomic structure give larger values than those given by Bragg, but the ratios for a column are much the same, as the following table, in which Cl is taken as unity, shows:—

| Element. | Rankine, viscosity. | Richards, compressibility. | Landé, at. structure. | Davy, X-rays. | Bragg, crystal. |
|---|---|---|---|---|---|
| Cl..... | 1·0 | 1·0 | 1·0 | 1·0 | 1·0 |
| Br ... | 1·11 | 1·07 | 1·12 | 1·11 | 1·13 |
| I ..... | 1·22 | 1·21 | 1·25 | 1·27 | 1·33 |

Thus estimates of the ratios of the radii by various observers differ by as much as 5 per cent. in some cases—that is, by something of the order of the discrepancies found in the present paper.

* Quoted by Grimm, *Zeits. f. Phys. Chem.* xcviii. p. 372 (Oct. 1921).

### V. *Values of the Constants for Columns.*

The constants expressing the quotients of the refractivities by the volumes for the various columns of the Periodic Table may be conveniently summarized by the use of a formula due to Mosotti *. Treating the atoms of a gas as perfectly conducting spheres, Mosotti found that:—

$$K-1=\tfrac{1}{2}\pi N^2\sigma^3,$$

where K is the dielectric capacity, N is the number of atoms per c.c., and $\sigma$ is the diameter of an atom.

This leads to a formula for the refractivity given by

$$\mu-1=\frac{\pi}{4}N\sigma^3=0{\cdot}79N\sigma^3.$$

If, therefore, a formula $\mu-1=KN\sigma^3$, where K is a constant for a given column, be employed, K is found to have the following values if N be taken as $2{\cdot}705\times10^{19}$

| Group..... | V. | VI. | VII. | 0. |
|---|---|---|---|---|
| | 5·07 | 4·68 | 3·04 | 1·23 |

The atoms of the inert gases provide the nearest approach to the Mosotti relation, and presumably to perfectly conducting spheres.

So far no simple law has been found for these numbers. Le Bas concluded that for the elements of a row the combined atomic refractivities were roughly proportional to the corresponding valencies. No such rule appears to hold for the numbers found, and it would be useful and interesting if these could be explained.

*Abstract.*

The refractivities of fifteen elements for sodium light have been plotted against the corresponding atomic volumes, calculated from the estimates of atomic diameters given by Prof. W. L. Bragg from his work on crystal structure. The elements of a vertical column of the Periodic Table when plotted on a graph fall upon a straight line, showing that the refractivity is proportional to the atomic volume, but the ratio $\frac{\text{refractivity}}{\text{volume}}$ decreases from left to right, *i. e.* in the direction of the decreasing valency. That the refractivities of the elements in the last four columns bear approximately

* Jeans's 'Electricity and Magnetism,' 4th ed. p. 130.

the same ratio to one another as noticed by Cuthbertson may possibly be explained by the fact that the atomic radii towards the end of a period have approximately the same value. The different constants obtained for $\frac{\text{refractivity}}{\text{volume}}$ for the various columns remain to be explained.

East London College,
Feb. 1924.

## LXXII. *On a Supposed Limitation of the Second Law of Thermodynamics.*

*To the Editors of the Philosophical Magazine.*

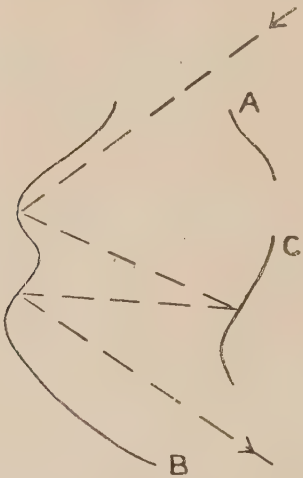
Gentlemen,—

In the January number of the Phil. Mag. for this year (p. 152) Witmer shows by a detailed analysis the fallacy existing in Fairbourne's proof of a limitation of the Second Law of Thermodynamics *. The idea was that vessels of certain shapes immersed in a gas, where the mean free path is large in comparison with the dimensions of the vessel, might cause a motion of the gas to take place in one preponderating direction. Witmer shows that this would not occur for the vessels dealt with by Fairbourne by working out in detail the paths of the reflected gas molecules. It seems worth while, however, to point out that the same may be proved generally for a vessel of any shape whatever by means of the following simple considerations.

Suppose we are dealing with a vessel of arbitrary shape and containing an arbitrary number of apertures A, B, C, etc. In the steady state the number of molecules entering the vessel in a given time must, on the average, be the same as the number leaving during the same period. This must be true whether the vessel creates a general stream of gas in one direction or not. A necessary consequence of this is that any gas molecule which enters the vessel from outside must emerge through one of the apertures after a finite number of collisions with the walls of the vessel; moreover, any path leading from A to B will be reversible and will serve to conduct molecules from B to A. We shall suppose the walls of the vessel to be smooth but otherwise of arbitrary curvature. Any element $d$S of the interior surface may therefore be considered as plane when its magnitude is decreased indefinitely. If now molecules contained within an elementary convergent or divergent bundle bounded by

* Phil. Mag. (6) xliii. p. 1047 (1922).

the solid angle $d\Omega$ be incident on $dS$ then, after reflexion, these molecules will be contained within an elementary bundle bounded by the same solid angle $d\Omega$; for, if $\theta$ be the angle between the normal to $dS$ and the direction of incidence of the bundle, we should have $d\Omega = \sin\theta\, d\theta\, d\phi$, where $\phi$ denotes the azimuth. After reflexion the element of solid angle would be $d\Omega' = \sin\theta'\, d\theta'\, d\phi' = d\Omega$, since, by




the laws of reflexion, $\theta = \theta'$, $\phi = \phi'$. The angular aperture therefore of such an elementary bundle will not be altered by reflexion. This will hold for any elementary bundle of molecules crossing an element of cross-section $dS$ of an aperture A and entering the vessel. Such a bundle emerging after a finite number of collisions from some other aperture, B say, will be bounded by the same solid angle. If the directions of motion of molecules outside the vessel are uniformly distributed in all directions, then the number of molecules the directions of motion of which are contained in a beam of given solid angle will be proportional to that solid angle, and one direction of motion will be just as probable as the opposite one.

It follows from this that no resultant motion of the gas molecules will occur in any of these elementary bundles, since the number of molecules entering the beam at B and moving to A will be the same, in any given time, as the number entering at A and moving to B. We may divide up each aperture into elements of cross-section, and the above considerations will apply to every bundle passing through one of these elements of area. It follows, therefore, that if the directions of the gas molecules outside any vessel are

distributed uniformly in all directions, then the same will hold in the steady state for any region in the interior of the vessel, since none of the bundles passing through an element of volume at the point under consideration will contribute anything to the motion of the gas as a whole. The above argument may easily be extended to the case where singularities occur in the surface such as sharp edges or points, and so the result is perfectly general.

In conclusion I wish to thank Prof. Richardson for kindly reading this note over before publication.

Physics Laboratory,
King's College, London. J. W. Fisher.

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## LXXIII. *Notices respecting New Books.*

*The Theory of Relativity: Three Lectures for Chemists.* By Erwin Freundlich, Director of the Einstein Tower. Translated by H. L. Brose, with an Introduction by Viscount Haldane. (Pp. xii+98.) (London: Methuen & Co., 1924. Price 5*s.* net.)

*The Foundations of Einstein's Theory of Gravitation.* By Erwin Freundlich. Translated by H. L. Brose, with a Preface by Albert Einstein and an Introduction by H. H. Turner. (Pp. xvi+140.) (London: Methuen & Co., 1924. Price 6*s.* net.)

In the preface to the second of these volumes, Prof. Einstein states that "the author has succeeded in rendering the fundamental ideas of the theory accessible to all who are to some extent conversant with the methods of reasoning of the exact sciences. The relations of the problem to mathematics, to the theory of knowledge, physics and astronomy are expounded in a fascinating style, and the depth of thought of Riemann, a mathematician so far in advance of his time, has in particular received warm appreciation." This is as complete and accurate a summary of the volume as it is possible to give in a brief compass. The English translation was first published in 1919 by the Cambridge University Press. The new edition is translated from the revised and enlarged German edition and contains, in addition, a number of notes by the author containing references to original literature and amplifying various points in the argument. Notes by the translator, entitled "On the Theory of Relativity" and "Some Aspects of Relativity: the Third Test" are also included.

The other volume under review covers somewhat similar ground, in briefer fashion, and omitting practically the whole account of the work of Riemann. It consists of three lectures delivered to a German Chemical Society, though the name of the Society and the dates of delivery are nowhere stated.

In both volumes special stress is laid on the fundamental importance for the generalized theory of the equality of inertial and gravitational mass. In many elementary expositions of the

theory, sufficient prominence is not given to this remarkable relationship.

Both volumes can be confidently recommended as providing brief, accurate and clearly expressed accounts of the ideas at the basis of relativity. The translations are in general good, though in the first volume, p. 35, "constellation" is employed in an unusual manner and it does not conduce to clarity to refer to the two components of a double star as the "star" and the "central body." On p. 37, "the relative motion of the telescope to the star" should read ". . . . to the light from the star."

*The Theory of Determinants in the Historical Order of Development.* Vol. IV. *The Period* 1880 *to* 1900. By Sir THOMAS MUIR, D.Sc., LL.D., F.R.S., C.M.G., formerly Superintendent-General of Education in Cape Colony. (Pp. xxxi+508.) (London: Macmillan & Co., 1923. Price 40*s.* net.)

THIS volume completes Sir Thomas Muir's monumental account of the historical development of the theory of determinants up to the year 1900. The first volume appeared as long ago as 1905 and the concluding volume has been passed through the press since the author's retirement. He is to be congratulated upon the successful completion of the task upon which he embarked many years ago. It originated in his discovery, when engaged upon his 'Treatise on the Theory of Determinants,' that much inaccurate statement prevailed in regard to the authorship and history of various theorems dealing with determinants. He therefore resolved to set about collecting the titles of all the writings which had appeared on the theory up to the end of 1880. This date was later extended to 1900.

The concluding volume follows the same general plan as the preceding volumes which have been reviewed in these pages, a plan which is well known to students of the subject. For purposes of reference the work is unique and as such it demands a place on the shelves of every scientific library. It is complete, as far as the author's extensive investigations can make it, in the sense that no paper which has contributed anything new to the theory is excluded. To each paper, the author has added an illuminating commentary. The mathematician can take up any one of these four volumes and open it at any page, and is sure to find something to interest him.

The completion of Sir Thomas Muir's work has long been looked forward to. The advances of nearly a quarter of a century since 1900 are, however, not dealt with in these volumes. Is it too much to hope that some other enthusiastic student of the subject will take up the task where Sir Thomas Muir has left it?

*Relativity and Gravitation.* By T. PERCY NUNN, M.A., D.Sc., Professor of Education in the University of London. (Pp. 167 with 10 figures.) (London: University of London Press, 1923. Price 6*s.* net.)

THIS work is intended to fill a gap between those books dealing with the Theory of Relativity which treat it from the popular

aspect and demand little or no mathematical equipment on the part of the reader and the advanced works which presuppose a somewhat extensive knowledge of mathematics. The standard of mathematical knowledge demanded of the reader is that of the B.Sc. pass degree and, wherever necessary, the mathematical demonstrations are given with sufficient detail for such a reader to pass without difficulty from step to step. The greatest difficulty which this class of reader is likely to find is in the assimilation of the basic ideas of the tensor calculus and, this subject not having been included in his course of studies, he finds its manipulation somewhat difficult. The author has therefore eased the way by establishing the "three crucial phenomena" without employing the tensor calculus. The method consists in determining the coefficients in the expression for $ds^2$ by consideration of their Galilean values, their values at infinity, and the value of the gravitational potential. Thus the phenomena which have attracted the interest of the 'educated world' are discussed in an easy way, the tensor calculus being developed subsequently.

We are of the opinion that the author has achieved his purpose with considerable success. For the person with little mathematical training or for those whose mathematics are rusty from long disuse, we cannot recommend any volume as more suitable for explaining the foundations of the theory and the principal results which follow from it.

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## LXXIV. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 624.]

February 27th, 1924.—Prof. W. W. Watts, Sc.D., F.R.S., Vice-President, in the Chair

THE following communication was read:—

'Age and Origin of the Lough Neagh Clays.' By William Bourke Wright, B.A., F.G.S.

The problem of the age and origin of the Lough Neagh Clays is of old standing. They have, by most geologists, been doubtfully referred to the Pliocene. Lack of exposure and the apparent absence of fossils precluded any exact determination of age. In 1918 a deep bore penetrated them from top to bottom, and smoothed out nearly all difficulties. Careful examination of the cores has enabled the author to draw the following conclusions:—

(1) The series has a thickness of over 1000 feet, and is subdivisible into:—
   - (*a*) Upper Clays and Sands.
   - (*b*) Middle Shales.
   - (*c*) Lower Clays and Sands.

(2) The age is Older Tertiary, not Pliocene. This is established by the presence of *Sequoia couttsiæ* Heer and three species of *Dewalquea*.

(3) The series has suffered about the same amount of folding and faulting as the basaltic lavas upon which it rests.

(4) A prolonged period of weathering separated the last outpouring of lava and the deposition of the clays.

(5) The result of this weathering has been the production of about 70 feet of lithomarge, which, being widely distributed over the catchment-areas of the tributary rivers, supplied the kaolin for the formation of the clays.

(6) The presence of abundant quartz-sand shows that the river-basins extended beyond the basaltic area.

(7) The Upper Basalt Lavas of Antrim and the underlying Interbasaltic Zone of Weathering, with its contained rhyolitic lavas, are preserved at least locally beneath the Lough Neagh Beds.

A mechanism can be suggested to account for the relatively iron-free nature of the sediments. As it is clear that the clays have been largely derived from the denudation of lithomarge, it is thought that the composition of the latter affords a clue. Lithomarge is largely a mixture of crystalline kaolin with colloidal iron and some bauxite; and it is regarded as probable that the iron, on account of its fine state of subdivision, remained in suspension in the lake, and was carried off over the outlet, while the coarser kaolin was deposited.

## LXXV. *Intelligence and Miscellaneous Articles.*

### INTERNATIONAL CONFERENCE ON APPLIED MECHANICS.

AN International Conference on Applied Mechanics will be held at Delft, Holland, on April 22nd to 26th. Two of these days will be assigned to sessions in which original communications will be read in the following sections:—(i.) Rational Mechanics; (ii.) The Theory of Elasticity; (iii.) Hydro- and Aero-dynamics (including Aeronautics). Two other days will be devoted to General Meetings for reviewing and discussing the following subjects:—(1) Graphical and numerical methods of solving differential equations; (2) Experimental methods of solving stress problems; (3) Stress problems in plastic media; (4) The theory of rupture; (5) The physical aspects of non-elastic deformations; (6) Friction and lubrication; (7) Motions in rotating fluids; (8) Stability of fluid motions; (9) Wave-motion; (10) The motion of a fluid in the boundary layer along the surface of solids: (11) The turbulence in the oceans and in the atmosphere; (12) The dynamics of the atmosphere.

Intending visitors are requested to communicate with one of the following members of the Executive Committee:—

Prof. C. B. Biezeno,
Prof. J. M. Burgers,
Prof. J. A. Schouten,

Laboratorium voor Aero- en Hydrodynamica
des Technische Hoogeschool,
Nieuwe Laan 76,
Delft.